



Capacitive carbon and electrochemical lead electrode systems at the negative plates of lead–acid batteries and elementary processes on cycling



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HIGHLIGHTS

- Capacitive carbon and electrochemical lead systems operate in NAM with carbon additives.
- The capacitive carbon system has small Ah capacity but high rate of operation.
- The electrochemical lead system is slow to accept charge but has high Ah capacity.
- Some carbons reduce the median pore radius of NAM to membrane sizes.
- Carbon additives alter the structure and may change the chemistry of negative plates.

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ABSTRACT

Batteries in hybrid electric vehicles operate in High-Rate Partial-State-of-Charge (HRPSOC) cycling duty. To make lead–acid batteries suitable for this duty, carbon is added to the negative active material. As a result of this technological change, two electrical systems form at the negative plates: (a) a *capacitive carbon system* comprising high-rate charging and discharging of the electric double layer; low Ah capacity, and (b) a *lead electrochemical system*, comprising oxidation of Pb to PbSO₄ during discharge and vice versa during charge; this system is slow to accept charge, but has high Ah capacity. Through cycling lead–acid cells under HRPSOC conditions with short current pulses of various durations we have established that the processes involved in the capacitive system proceed highly reversibly and complete hundreds of thousands HRPSOC cycles. The number of cycles achieved by the electrochemical system is limited to tens of thousands and lead to progressive sulfation. Carbon added to the negative active material changes the latter's structure. The specific surface of NAM increases and the median pore radius decreases. Some carbon additives may reduce the radius of the pores in NAM to membrane sizes, which may change the chemistry of the electrochemical system.

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1. Introduction

Every time a demand for a new type of portable or reserve energy source emerges, lead–acid batteries face challenges that require novel technological and/or design solutions. Such was the case with hybrid electric vehicles (HEV), too. Batteries in HEV applications operate from partial state of charge and experience short charge and discharge events with high currents (High-Rate Partial-State-of-Charge cycling duty) and regenerative braking. This new operating mode seems to be quite a challenge for existing

lead–acid batteries, because of the relatively low specific surface area of the negative active mass, which limits its charge acceptance. Besides, when operated from partial state of charge, the negative plates get progressively sulfated. In order to meet the requirements of the HRPSOC operating mode, the lead–acid battery technology has to be changed.

Nakamura, Shiomi and collaborators [1,2] have established that introduction of higher loadings of carbon black to the negative active material improves substantially the charge acceptance and retards sulfation of the negative plates during the simulated HRPSOC test of batteries for hybrid electric vehicle (HEV) applications. Several hypotheses are proposed in the literature for the action of carbons on the HRPSOC performance of the batteries [1–7]. Moseley has summarized these mechanisms in a review published in the *Journal of Power Sources* [8].

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Table 1

Characteristics (as specified by supplier) of the carbon materials used as additives to NAM in the present study

Symbol	Product name/supplier	Type of material	Particle size	BET surface, $\text{m}^2 \text{g}^{-1}$
TDA	SO-15A, TDA Research	Activated carbon	<44 μm	1615
AC3	Black Pearls-2000, Cabot Corp.	Carbon black	12 nm	1475

Based on experimental data obtained within ALABC sponsored projects, we have proposed a new mechanism of carbon action. We have established that, during cycling of cells under HRPSoc conditions, the electrochemical and chemical processes at the negative plates proceed not only on the lead surface, but on the surface of the carbon phase as well [9]. Thus, carbon particles in NAM are involved in the current generation and accumulation processes. Furthermore, it has been found that carbons exert an influence on the structure of the lead negative active mass [10,11]. But is the role of carbon additives in the negative plates exhausted with the above mentioned functions?

In an attempt to make lead–acid batteries suitable for HEV applications, battery researchers and engineers have tried various innovative cell design solutions. Lam and collaborators, in cooperation with Furukawa et al., have replaced the conventional negative plates with plates comprising half regular sponge lead plate and half carbon super-capacitor plate [12,13]. This battery, called the UltraBattery™, combines the features of an electrochemical power source with those of an electric capacitor.

When higher loadings of carbon are added to the negative active material, the question arises whether this additive does not create a capacitive energy source component with its own specific effect on battery performance? Does not the carbon additive have its own contribution to the capacity of the negative electrode apart from that of the electrochemical lead electrode system?

The aim of the present paper is to find the answers to the above questions. To achieve this aim we set lead–acid cells with carbon additives in NAM to high-rate cycling with short pulses of various durations. This approach allowed us to distinguish between the capacitive processes on the carbon surface and the electrochemical processes on the lead surface, and thus to identify the elementary processes that take place at the negative plates on HRPSoc cycling.

2. Experimental

2.1. Negative plate preparation

The effects of two carbon materials were investigated: TDA (SO-15A activated carbon, supplied by TDA Research Inc.) and AC3 (Black Pearls-2000 carbon black, supplied by Cabot Corp.). Table 1 summarizes the characteristics (as specified by the suppliers) of the two carbon materials used. TDA carbon comprises particles up to 44 μm in size and AC3 carbon is a fine powder with 12 nm primary particle size. These two types of carbons were selected because of the great difference in particle size.

The negative pastes were prepared using H_2SO_4 and leady oxide (LO) at a ratio of 4.5% by weight. The concentration of BaSO_4 was 0.8 wt% (versus the LO). Two types of carbon materials were used as additives in concentrations 0.5 wt% or 2.0 wt% for TDA, or 0.5 wt% or 1.0 wt% for AC3, respectively. These pastes were used to prepare negative plates with PbCaSn grids. The plates were formed in 1.06 s.g. H_2SO_4 solution. Samples of the formed negative active material were characterized by X-ray diffraction analysis, scanning electron microscopy and Hg porosimetry.

2.2. Test cell design

Lead–acid test cells (2 V/4.5 Ah) were assembled comprising two negative and three oversized positive plates separated by 3 mm thick AGM separator (supplied by Hollingsworth & Vose). The active block comprising plates and separators was compressed so that the separator thickness was reduced by 20%. The cells were flooded with 80 ml H_2SO_4 solution of 1.28 s.g. (the electrolyte forming a “mirror” over the plates) and sealed. The rated capacity of the test cells at 20 h discharge rate (C_{20}) was calculated at 50% utilization of the negative active mass.

2.3. Test program

In order to identify the elementary processes during battery charge and discharge the test cells were subjected to cycling with charge and discharge pulses of different duration, i.e. to different depths of discharge. The time of rest between the pulses was also varied.

The test cell performance under simulated HRPSoc conditions was evaluated using a simplified profile imitating the micro-hybrid driving mode. This cycling mode has been generally adopted for projects implemented within the ALABC program. The first step in this cycling profile was discharge at $I = 1 \text{ C}$ A rate to 50% SoC. After that, the cells were subjected to cycling according to the following schedule: charge at 4C rate for 5 s, 30 s or 50 s, rest for 1 s, 10 s or 60 s, discharge at 4C rate for 5 s, 30 s or 50 s, rest for 1 s, 10 s or 60 s. 1C and 4C are the currents for 1 h and 0.25 h discharge rate, respectively, as determined from the Peukert plot. All tests were conducted at 25 °C.

During these tests, the plates were cycled at 0.5 %, 3.0% or 5.0% depth of discharge within each micro-cycle, starting from 50% SoC. The cell voltage was measured at the end of the charge and discharge pulses, and the test was stopped when the end-of-discharge cell voltage fell down to 1.83 V (for 0.5% and 3.0% DoD) or to 1.70 V (for 5.0% DoD), or when the upper end-of-charge voltage limit of 2.83 V (for all DoD) was reached. The above described cycling steps comprised one cycle-set of the HRPSoc test. The cells were fully re-charged and their C_{20} capacity was measured. Then the cells were discharged with 1C A to 50% SoC and a new cycle-set followed. In some cases the negative plate potential was also measured versus $\text{Ag}/\text{Ag}_2\text{SO}_4$ reference electrode during the cycling test. The test cells were subjected to up to 3 cycle-sets.

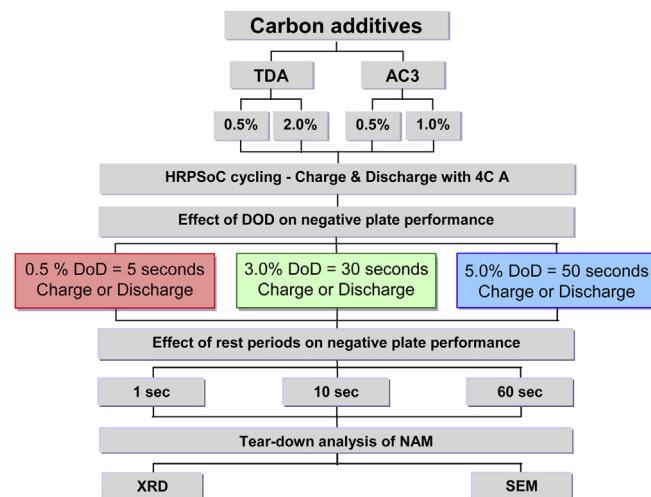


Fig. 1. Summary of the negative plate variants used in this study and of the types of tests performed.

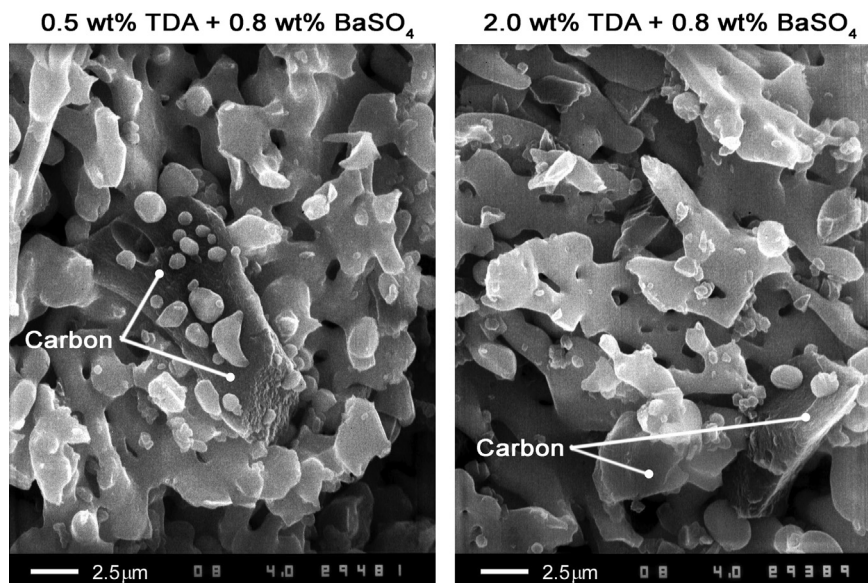


Fig. 2. SEM images of NAM with 0.5 wt% or 2.0 wt% TDA activated carbon.

On completion of the cycling test, samples of the negative active mass were set to SEM examination and its phase composition was characterized by XRD analysis.

Fig. 1 presents schematically a summary of the variety of negative plates prepared with the two types of carbons in different concentrations and of the types of tests and analyses performed within this study.

3. Experimental results

3.1. Microstructure and crystal morphology of NAM with different carbon additives

First the influence of carbons on the structure of the negative active mass was studied. SEM images of the NAM structures with TDA added in two concentrations (0.5 wt% or 2.0 wt%) are presented in Fig. 2.

TDA particles are big in size and are integrated in the skeletal structure of NAM. Lead nuclei are formed on the surface of the TDA particles. These nuclei grow and merge forming new lead branches. Thus, the TDA carbon particles get incorporated into the NAM structure and become an integral part of it.

Fig. 3 features the crystal morphology of NAM samples from the interior of negative plates containing 0.5 wt% or 1.0 wt% AC3 carbon black. The lead particles are mostly spheroidal in shape. AC3 particles are very small and are adsorbed on the surface of the lead grains. Addition of 1.0 wt% AC3 to NAM reduces the size of the Pb grains and some changes in the microstructure of NAM occur.

If we compare the SEM images in Figs. 2 and 3 we will notice that TDA activated carbon and AC3 carbon black have different impact on the structural characteristics of the negative active mass. Hence, Pb + carbon/electrolyte interfaces with different electrochemical properties are formed, which will affect the electrochemical parameters of the cells.

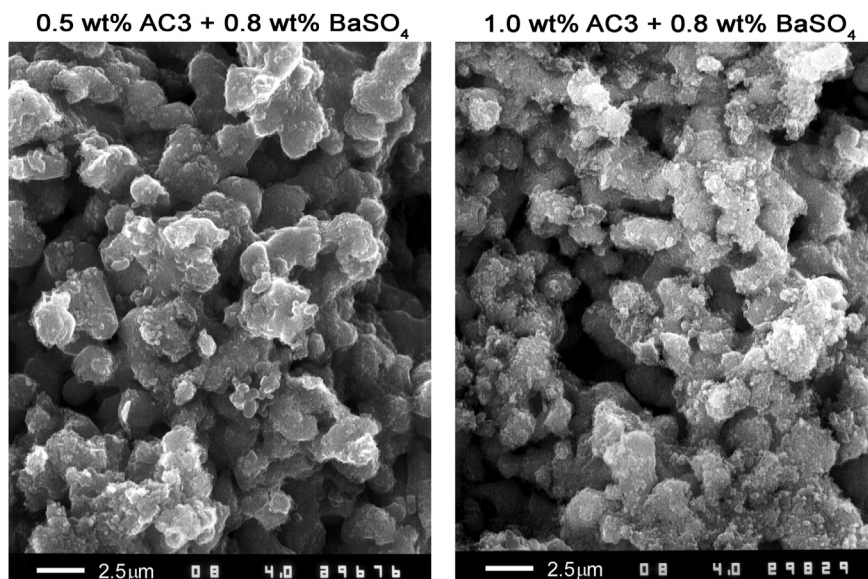


Fig. 3. SEM images of NAM with 0.5 wt% or 1.0 wt% AC3 carbon black.

3.2. Hg porosimetry measurements of NAM with different carbon additives

Fig. 4 illustrates the changes in cumulative pore volume as a function of pore radius for negative active masses with different loads of TDA activated carbon or AC3 carbon black. The measured total pore volume and median pore radius are also given in the figure.

The changes in carbon type and loading level in NAM reflect in changes in pore radius distribution. TDA activated carbon, when added in concentration 0.5 wt%, causes formation of large pores in NAM (7.25 μm pore radius). Addition of 2.0 wt% TDA reduces the median pore radius, from 7.25 μm to 2.44 μm . TDA carbon additive does not change much the total pore volume of NAM.

On the contrary, addition of only 0.5 wt% AC3 leads to formation of very small pores (1.10 μm) in NAM. Further increase of the AC3 loading level to 1.0 wt% reduces the pore size to 0.55 μm , i.e. the negative active mass acquires membrane-sized pore structure.

The specific BET surface area of NAM samples with different compositions was measured. The measured specific surface area of NAM with 0.5 wt% TDA is $5.80 \text{ m}^2 \text{ g}^{-1}$ and when the TDA carbon load is increased to 2.0 wt%, the BET surface area increases to $25.20 \text{ m}^2 \text{ g}^{-1}$. The respective BET surface area values for the NAM samples with AC3 carbon black are $4.70 \text{ m}^2 \text{ g}^{-1}$ for 0.5 wt% AC3 loading level and $8.75 \text{ m}^2 \text{ g}^{-1}$ for 1.0 wt% AC3 content in NAM. These results indicate that the surface area of NAM is strongly influenced by the type and amount of carbon added to it.

The above discussed porometric and BET surface data indicate clearly that *carbons added to the negative active mass alter its structure and pore system*. This will affect the transport and composition of the ionic flows into NAM and hence, the electrical performance parameters of the negative plates.

3.3. Electrochemical tests of cells with TDA activated carbon in NAM

3.3.1. Peukert dependences

Fig. 5 presents the obtained Peukert dependences for cells with negative plates containing two different concentrations of TDA activated carbon in NAM.

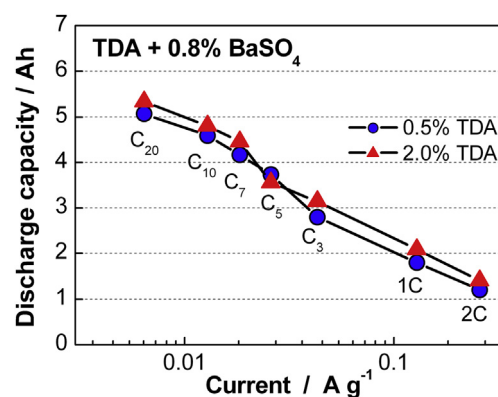


Fig. 5. Peukert dependences for cells with 0.5 wt% or 2.0 wt% TDA activated carbon in NAM.

The cell with 2.0 wt% TDA added to NAM has higher capacity within the whole range of current rates. Only at discharge current $i = C_5$ A, the cells with the two TDA concentrations (0.5 wt% and 2.0 wt%) have similar capacities.

3.3.2. HRPSoc cycling tests

First, test cells with 0.5 wt% or 2.0 wt% TDA in NAM were cycled at 0.5% depth of discharge (i.e. with 5 s pulses). The changes in negative plate potential within one micro-cycle were registered at the beginning, in the middle and at the end of the first cycle-set of the HRPSoc cycling test. The obtained results are presented in Fig. 6. ϕ_{OCV} stands for the open circuit potential and $\Delta\phi_C$ and $\Delta\phi_A$ are the cathodic and anodic polarizations within one charge–discharge micro-cycle.

With increase of the number of completed cycles the cathodic polarization ($\Delta\phi_C$) and the anodic polarization ($\Delta\phi_A$) increase slightly, which indicates that the processes that take place are highly reversible.

Fig. 7 illustrates the changes in negative plate potential within one 50 s micro-cycle for cells with 0.5 wt% or 2.0 wt% TDA in NAM cycled at 5.0% DoD. The negative plate potentials were measured at

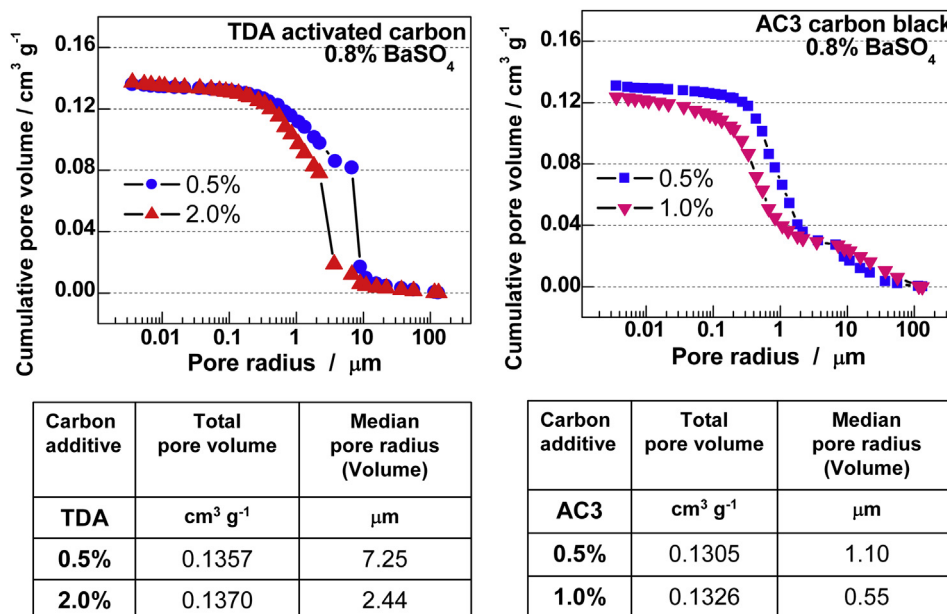
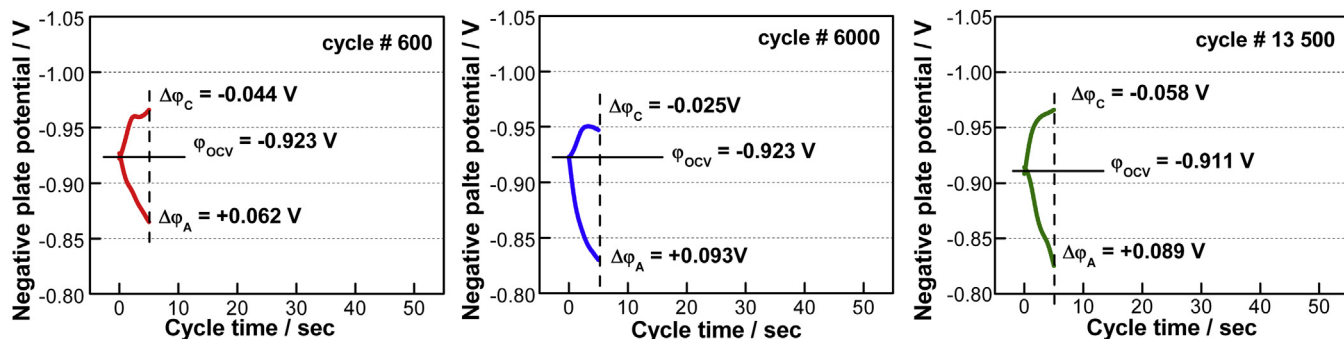


Fig. 4. Porometric data for NAM samples with TDA or AC3 carbon additives.

0.5% TDA + 0.8% BaSO₄; 0.5% DoD; I = 1.4 C₂₀ A; first cycle-set; rest – 10 sec



2.0% TDA + 0.8% BaSO₄; 0.5% DoD; I = 1.4 C₂₀ A; first cycle-set; rest – 10 sec

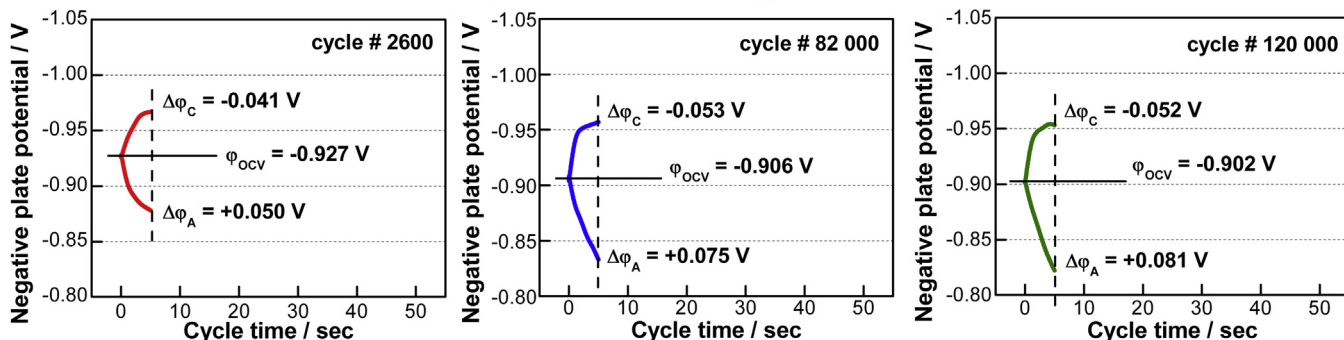
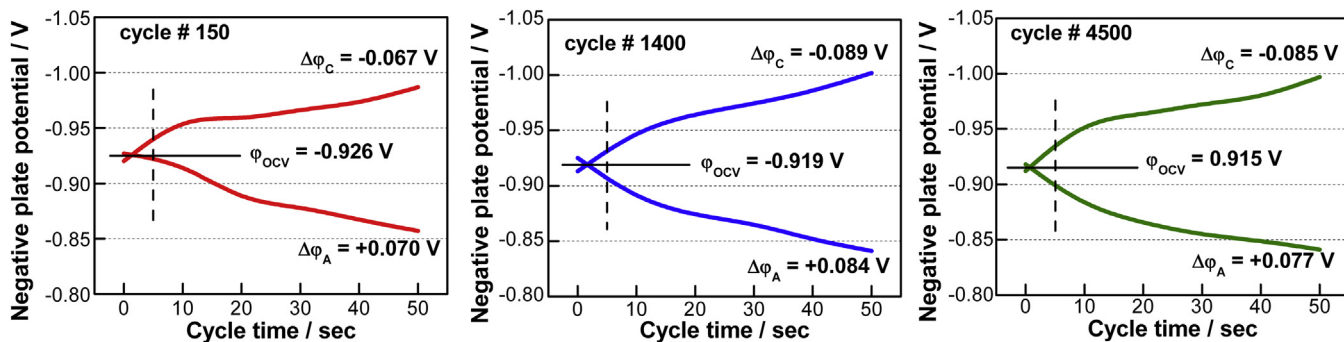


Fig. 6. Changes in negative plate potential within one micro-cycle as a function of polarization time for cells with 0.5 wt% or 2.0 wt% TDA in NAM cycled at 0.5% DoD (5 s pulses).

0.5% TDA + 0.8% BaSO₄; 5.0% DoD; I = 1.4 C₂₀ A; first cycle-set; rest – 10 sec



2.0% TDA + 0.8% BaSO₄; 5.0% DoD; I = 1.4 C₂₀ A; first cycle-set; rest – 10 sec

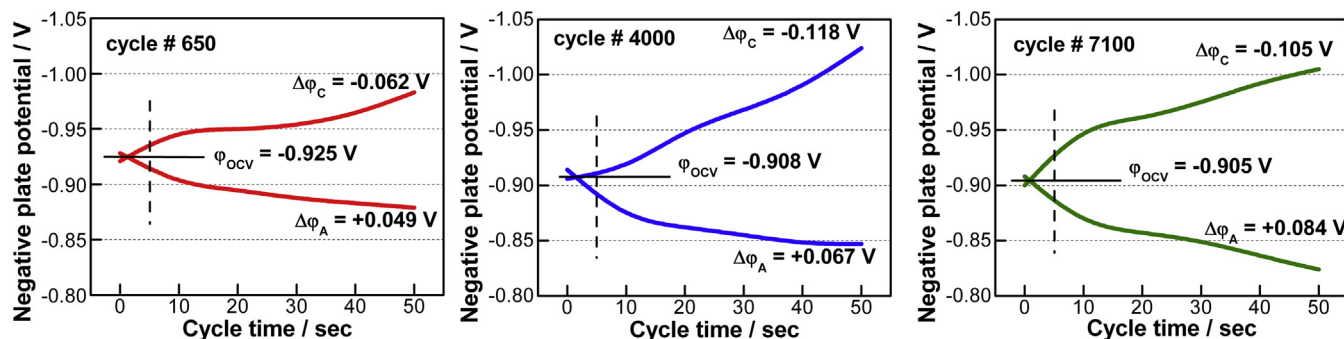


Fig. 7. Changes in negative plate potential within one micro-cycle as a function of polarization time for cells with 0.5 wt% or 2.0 wt% TDA in NAM cycled at 5.0% DoD (50 s pulses).

the beginning, in the middle and at the end of the first cycle-set of the HRPSoC cycling test.

Here, the polarization of the negative electrodes increases with increase of the number of completed cycles and the cells have a much lower cycleability (by several factors) within one cycle-set than the cells cycled at 0.5% DoD. This indicates that different processes occur during cycling at the two depths of discharge which lead to polarization of the negative plates.

Fig. 8 compares the negative plate potential/time curves (within one micro-cycle) for cells cycled with 5 s, 30 s or 50 s pulses (i.e. at 0.5%, 3.0% or 5.0% DoD). The curves for the cells cycled with 30 and 50 s pulses are similar in profile, but differ substantially from the potential/time dependences recorded on cycling with shorter pulses (5 s). These results are an illustration of the different types of processes that take place on cycling with current pulses of different duration.

On cycling with 5 s pulses, it can be presumed that mainly processes of charging and discharging of the electric double layer on the electrode surface proceed. Since the carbon surface exceeds

by far that of the lead phase, the potential changes within one micro-cycle will be determined by the charge accepted by the carbon surface. This means that the electrode behaves like a capacitor, i.e. it is rapidly charged and discharged. Within these short pulses, the role of electrochemical reactions, if any, will not be potential determining.

When the test cells are cycled with 30 or 50 s current pulses, there is enough time for the electrochemical and chemical reactions of lead oxidation to Pb^{2+} ions and the subsequent reaction between Pb^{2+} and SO_4^{2-} ions producing PbSO_4 to proceed during the anodic polarization. Then, during the cathodic polarization, the reverse reactions of PbSO_4 reduction to Pb take place.

If the above two processes are considered from a phenomenological point of view, it can be concluded that two electrical systems operate in the negative active mass:

- a capacitive system comprising charging and discharging of the electric double layer, mostly on the carbon surface; this system operates on cycling with 5 s pulses;

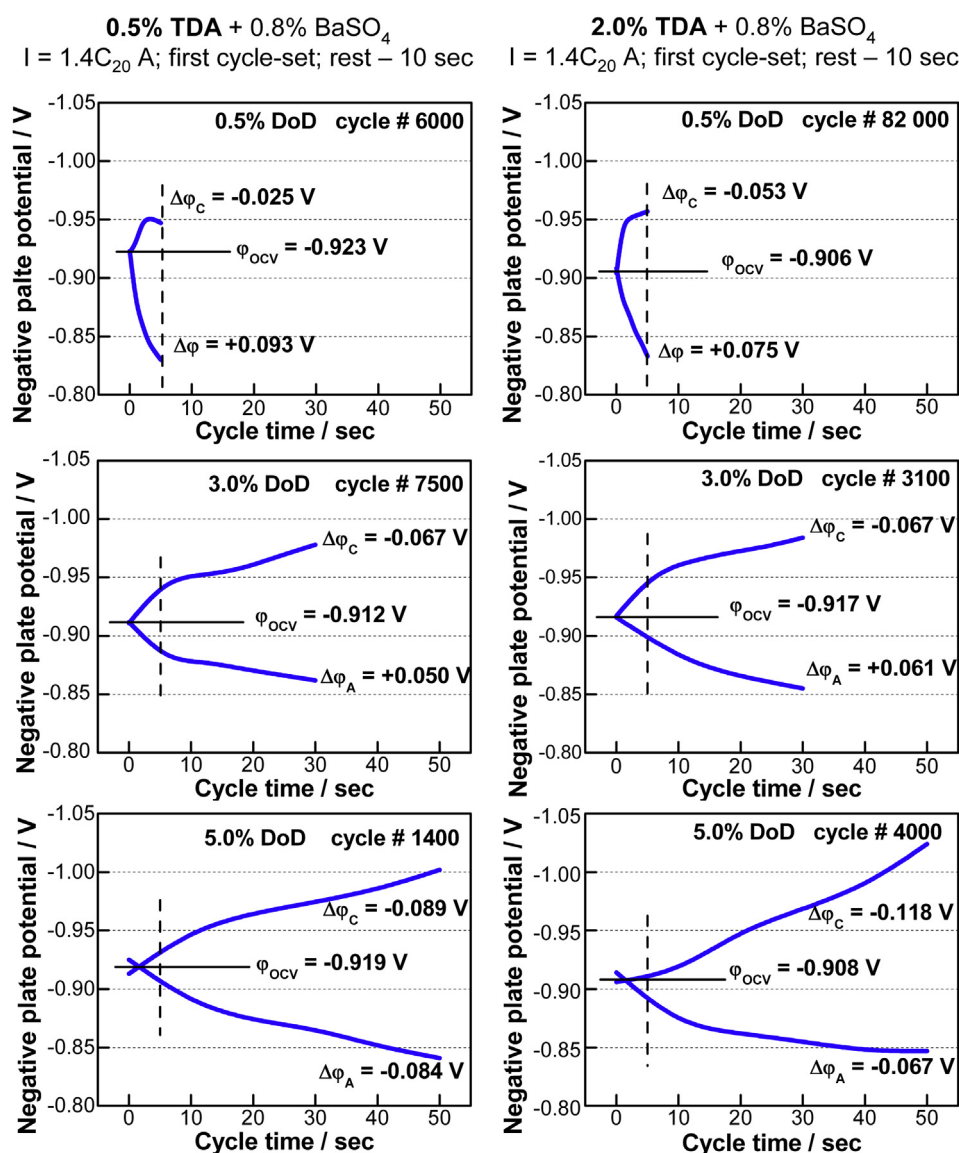


Fig. 8. Changes in negative plate potential within one micro-cycle as a function of polarization time for cells with 0.5 wt% or 2.0 wt% TDA in NAM cycled at three different depths of discharge.

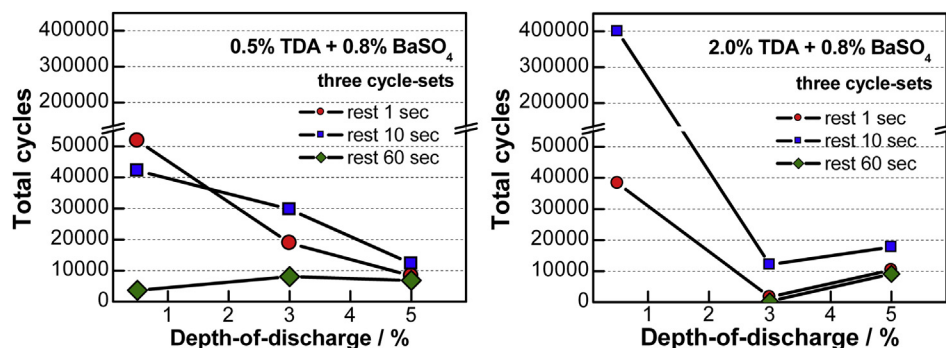


Fig. 9. HRPSoC cycling test results for cells with TDA carbon in NAM at three different depths of discharge.

(b) an electrochemical system comprising electrochemical and chemical reactions of Pb oxidation to PbSO_4 and the latter's subsequent reduction back to Pb; this system operates on cycling with longer charge and discharge current pulses (30 s or 50 s).

3.3.3. Cycleability of the test cells with TDA activated carbon in NAM at different depths of discharge

Fig. 9 compares the results of the simulated HRPSoC cycling tests for cells with 0.5 wt% or 2.0 wt% TDA activated carbon in NAM for three different depths of discharge (DoD) and three rest period durations. The figure summarizes the data for the total number of completed cycles for three cycle-sets as a function of DoD and rest period duration.

The data in the figure indicate that the total number of completed HRPSoC cycles depends very strongly both on the depth of discharge and on the TDA content in NAM. The cells cycled at 0.5% DoD have the best cycleability. When the DoD is increased to 3.0% or to 5.0%, the total number of cycles decreases abruptly.

If we compare the cycleability of the test cells with the two TDA concentrations when cycled at 0.5% DoD, it can be seen that the cells with 2.0 wt% TDA complete 400,000 cycles within three consecutive cycle-sets against only about 40,000 cycles for the cells

with 0.5 wt% TDA in NAM. This substantial difference in cycleability suggests that TDA carbon particles are involved directly in the cycling processes during the first five seconds.

3.3.4. Changes in cycleability from cycle-set to cycle-set

Fig. 10 shows the number of completed cycles per cycle-set for three consecutive cycle-sets as a function of the DoD and of the duration of the open circuit rest periods for cells with 0.5 wt% TDA in NAM.

When cycling is conducted with 5 s pulses and 1 or 10 s rest periods, the cycleability per cycle-set is high and changes but very slightly for the three consecutive cycle-sets. Under these conditions, the processes of capacitive charging and discharging of the electric double layer proceed on the carbon and lead surfaces almost reversibly. The observed decrease in cycleability when prolonging the open circuit rest periods indicates that even within the 5 s current pulses sulfation of the electrode surface proceeds, though at a low rate.

When the test cells are cycled with 30 or 50 s pulses, the number of micro-cycles they complete per cycle-set decreases from cycle-set to cycle-set. In this case, PbSO_4 progressively accumulates in the negative plates, which leads to their sulfation. The latter process is accelerated when the open circuit rest periods are extended. The processes of lead sulfate nucleation and crystal

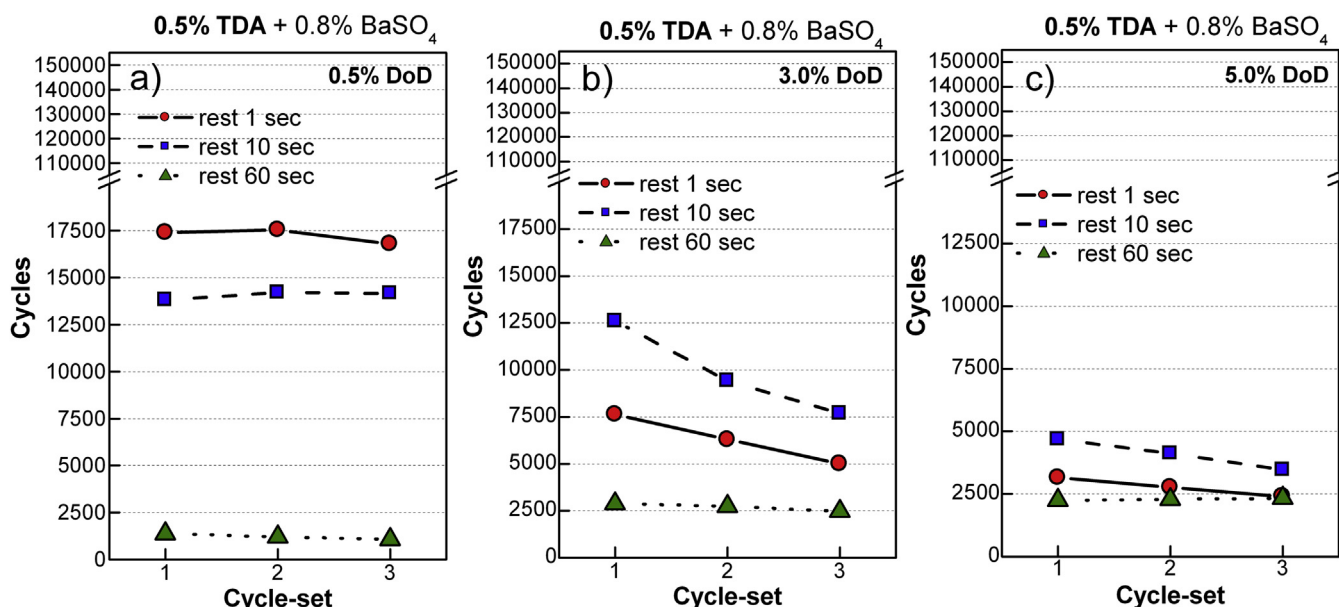


Fig. 10. Completed cycles per cycle-set as a function of DoD and rest periods duration for cells with 0.5% TDA carbon in NAM.

growth progress to an advanced stage when the duration of the current pulses and of the rest periods is increased. An interesting finding is that the cells cycled at 3.0 or 5.0% DoD exhibit the best cycleability when the time of rest between the charge and discharge pulses is 10 s. It is even better than that on cycling with 1 s rest periods. This indicates that the PbSO_4 particles formed during the 10 s rest period dissolve more readily and participate in the subsequent electrochemical reaction of lead formation.

3.3.5. Structure of NAM with TDA activated carbon after 3 cycle-sets of the HRPSOC cycling test

After the end of the third cycle-set, the test cells were charged and cut open. The negative plates were taken out of the cells, washed and dried in nitrogen atmosphere. Samples were taken from the surface and from the bulk of the negative active mass and set to SEM examinations. The SEM images in Fig. 11 show the structure of the superficial and the inner NAM layers.

The SEM pictures evidence clearly that the lead particles in the two NAM zones have changed their size during the cycling test, those in the surface NAM layers are significantly smaller than the particles in the bulk of NAM. The boundary between the two NAM zones can be seen in the SEM image in Fig. 11e.

If we compare the SEM images featuring the structure of NAM at different depths of discharge, it can be seen that at higher DoD a great number of particles in the surface NAM layers are interconnected into agglomerates with pores inbetween.

Fig. 12 shows SEM pictures of samples of NAM with 2.0 wt% TDA taken from the surface and from the interior of the plate. Here again, the surface NAM layers comprise smaller lead particles than those in the bulk of NAM. When cycled at 5.0% DoD, the structure of the surface NAM layer is built of aggregates of a huge number of interconnected lead particles with macropores between the aggregates. The SEM image of the NAM sample cycled at 3.0% DoD features the onset of formation of such aggregates. Obviously, with

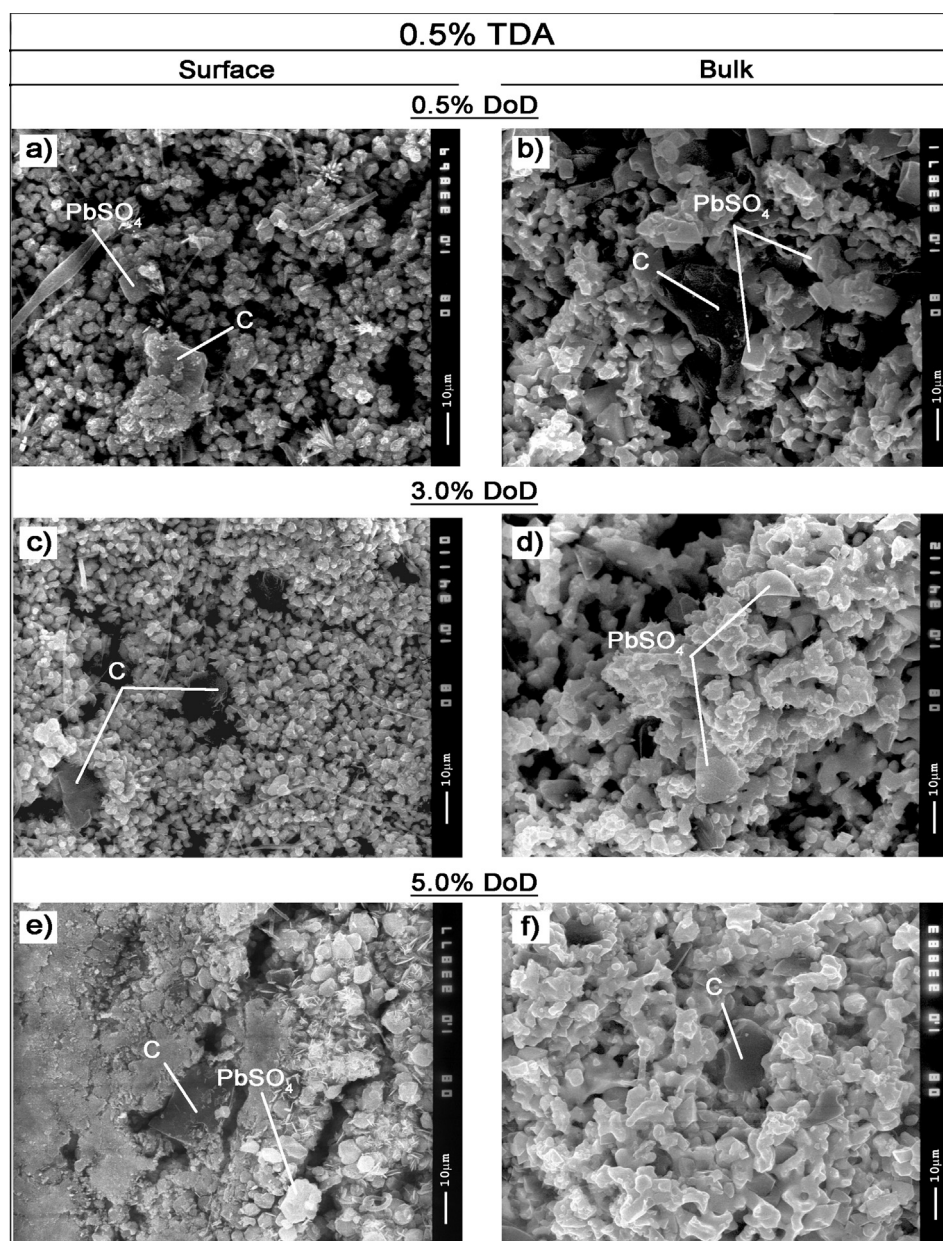


Fig. 11. Structure of NAM with 0.5 wt% TDA after cycling at 0.5%, 3.0% or 5.0% DoD. (a, c, e) NAM surface layer; (b, d, f) NAM sample from plate interior.

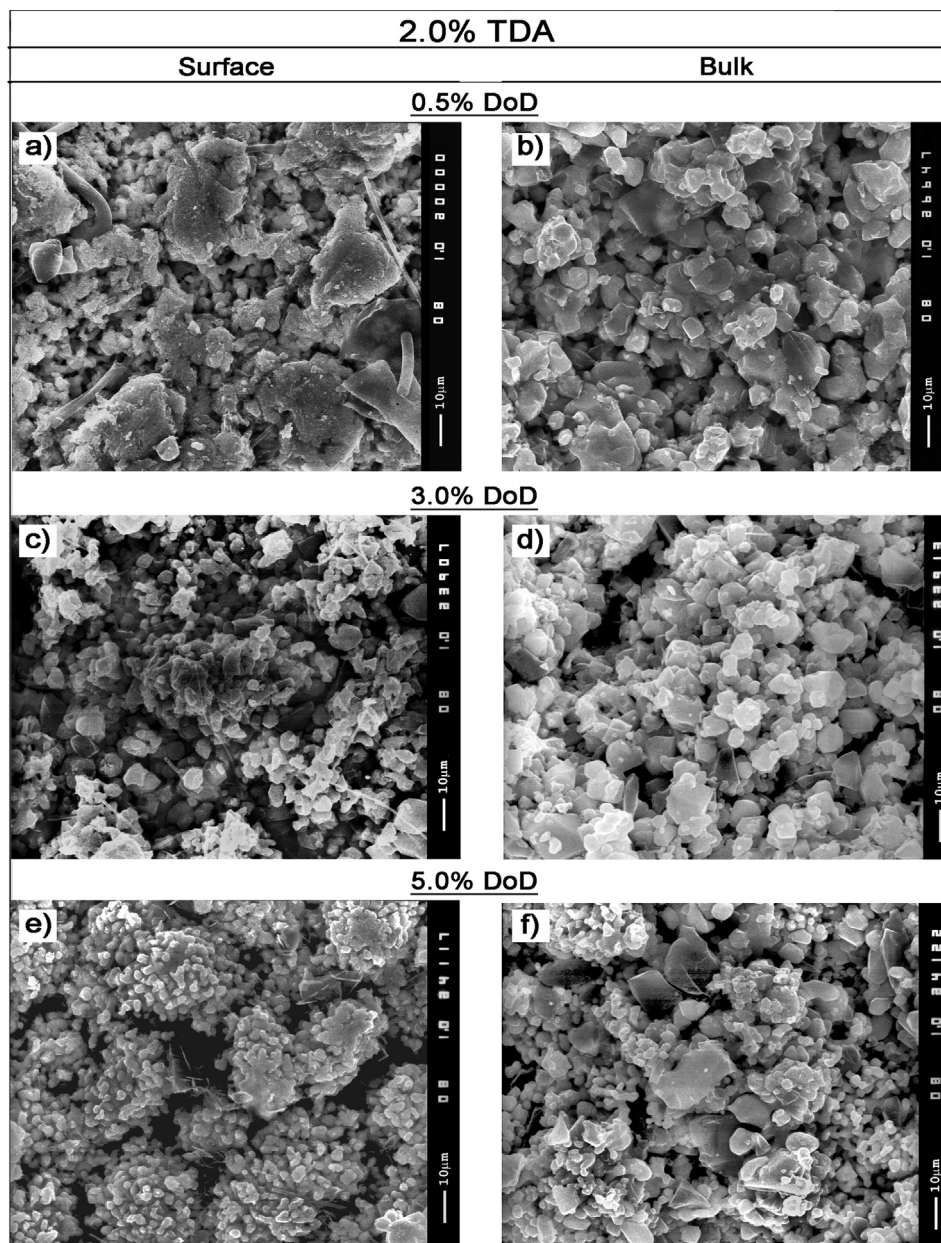


Fig. 12. Structure of NAM with 2.0 wt% TDA after cycling at 0.5%, 3.0% or 5.0% DoD. (a, c, e) NAM surface layer; (b, d, f) NAM sample from plate interior.

increase of the current pulse duration formation of such aggregates in the surface NAM layers is facilitated. Comparing the SEM images in Figs. 11 and 12 it can be seen that at 0.5 wt% TDA in NAM the agglomerates are built of numerous small lead particles, whereas the NAM with 2.0 wt% TDA comprises better shaped aggregates built of bigger particles. Higher loads of TDA activated carbon in NAM alter its macrostructure and accelerate the formation of aggregates.

3.3.6. Phase composition of NAM with TDA activated carbon after 3 cycle-sets of the HRPSOC cycling test, as determined by XRD analysis

Samples of the negative active mass of the different test cells were characterized by X-ray diffraction analysis. Fig. 13 shows the obtained X-ray diffraction patterns for the negative active mass with 0.5 wt% TDA activated carbon after cycling at 0.5%, 3.0% or 5.0% DoD. Quite similar XRD patterns are also obtained for the samples with 2.0 wt% TDA in NAM.

The plates are partially sulfated, irrespective of the cycling mode. The least affected by sulfation are the plates cycled at 3.0% DoD, followed by those cycled at 0.5% DoD. The cell cycled at 0.5% DoD exhibits the best cycleability within the three HRPSOC cycle-sets (a total of 400,000 cycles). The presence of PbSO_4 in NAM indicates that electrochemical and chemical processes of PbSO_4 formation and reduction proceed, too, but at a very low rate, which explains the great number of cycles completed by this cell. It is true that the cell was discharged to 50% SoC prior to the cycling test and the obtained PbSO_4 crystals have recrystallized. But the fact that the NAM samples from the three test cells contain different amounts of PbSO_4 after cycling indicates that formation and reduction of the lead sulfate phase, i.e. its recrystallization, proceed during the cycling test as well. Part of the lead sulfate formed on cycling is reduced during the cathodic polarization of the plates and another, though a small, part remains unreduced. As a result of recrystallization processes the remaining PbSO_4 crystals grow forming a

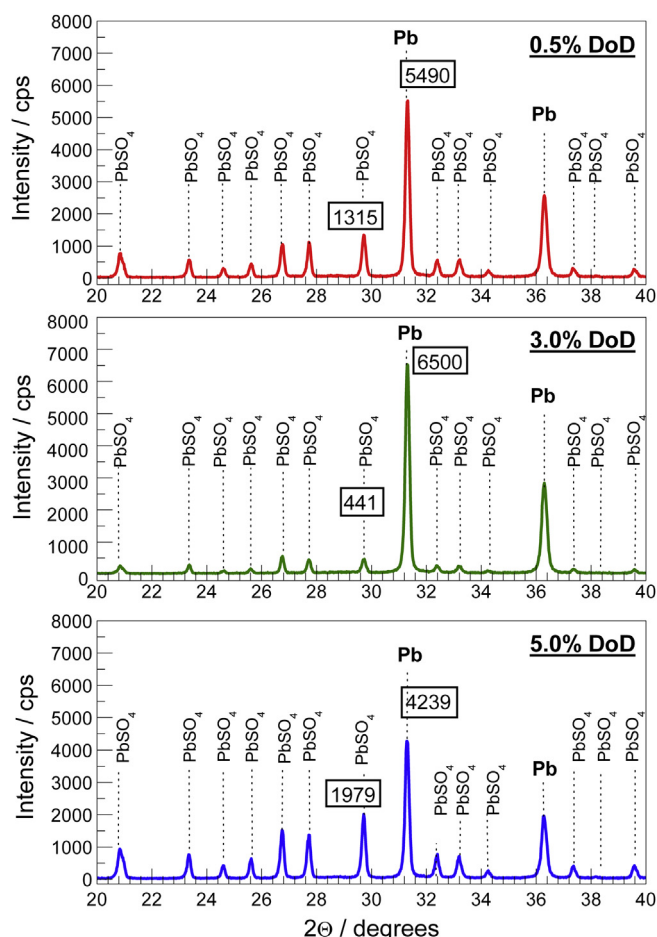


Fig. 13. X-ray diffraction patterns for the negative active mass with 0.5 wt% TDA activated carbon after cycling at 0.5%, 3.0% or 5.0% DoD.

separate phase composed of big PbSO_4 crystals in NAM. Even after re-charging the cells after the cycling test, considerable amounts of big PbSO_4 crystals remain unreduced.

3.4. Electrochemical tests of cells with AC3 carbon black added to NAM

3.4.1. Peukert dependences

Fig. 14 presents the Peukert plots for cells with negative plates with AC3 carbon black added to NAM in two different concentrations.

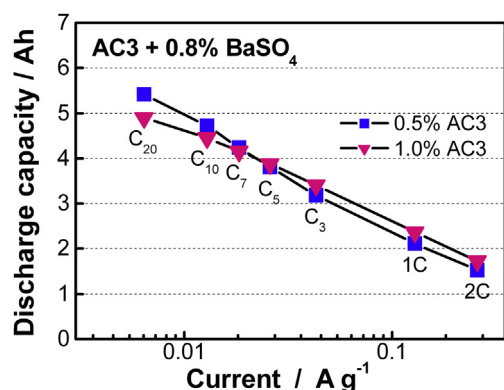


Fig. 14. Peukert dependences for cells with 0.5 wt% or 1.0 wt% AC3 carbon black in NAM.

When AC3 carbon black is used as additive to NAM, the cells with 0.5 wt% AC3 have higher capacity than those with 1.0 wt% AC3 content within the current range from $i = C_{20}$ A to $i = C_5$ A. At discharge currents between $i = C_5$ A and $i = 2C$ A, the cells with 1.0 wt% AC3 have higher capacity than those with the lower carbon content (0.5 wt%). Here again, the cells with the two carbon concentrations have equal or very close capacities when discharged with $i = C_5$ A, as in the case with TDA carbon additive in NAM (see Fig. 5).

3.4.2. Changes in potential of the negative plates within one micro-cycle for cells with 0.5 wt% or 1.0 wt% AC3 carbon black in NAM cycled at 0.5% or 5.0% DoD

Fig. 15 shows the changes in negative plate potential within one micro-cycle registered at the beginning, in the middle and at the end of the first cycle-set of the HRPSoC test, for cells with 0.5 wt% or 1.0 wt% AC3, cycled at 0.5% DoD (5 s pulses).

Within the first 600 cycles, the measured anodic and cathodic polarization of the cell with 0.5 wt% AC3 is almost equal. With increase of the number of completed cycles (55,000 cycles in the middle and 105,000 cycles at the end of the cycle-set) the anodic polarization increases compared to the cathodic polarization (97 mV anodic versus 71 mV cathodic polarization).

When the AC3 content in NAM is increased to 1.0 wt%, the obtained potential/time curves differ substantially. In this case, both the cathodic and anodic polarizations increase on cycling at almost equal rates (35,000 cycles). This polarization increase is much faster as compared to that for the cells with 0.5 wt% AC3.

Fig. 16 illustrates the changes in negative plate potential within one micro-cycle for cells with 0.5 wt% or 1.0 wt% AC3 cycled at 5.0% DoD.

The polarization curves obtained on cycling at 5.0% DoD differ substantially from those at the lower depth of discharge (0.5% DoD) reflecting different phenomena that govern the behavior of the negative electrodes.

The polarization of the negative plates with both AC3 concentrations increases with cycling, more significantly in the cells with the higher AC3 loading level (1.0 wt%). Bearing in mind that AC3 carbon black is a fine powder which adsorbs onto the lead surface and changes its structure, it can be presumed that such a structure of the interface impedes not only the electrochemical and chemical processes, but also the capacitive charging and discharging of the NAM surface as well. The observed rise in electrode polarization will reduce the number of completed cycles per cycle-set. On cycling at 5.0% DoD, the measured cathodic or anodic polarization of the negative plates with 0.5 wt% AC3 is about 125 mV at the end of the first cycle-set (i.e. after 2100 cycles), whereas in the cells with 1.0 wt% AC3, the cathodic polarization is much higher than the anodic one after 4700 cycles.

3.4.3. Cycleability of cells with AC3 carbon black in NAM at different depths of discharge

Fig. 17 compares the results of the HRPSoC cycling tests of cells with 0.5% or 1.0% AC3 carbon black in NAM for three different depths of discharge. The figure presents the total number of completed HRPSoC cycles for three consecutive cycle-sets as a function of DoD and rest periods duration. Cycling was conducted at a current rate of 2C A, as determined from the Peukert curves.

The graphs in Fig. 17 indicate that with increase of the depth of discharge from 0.5% to 3.0% or 5.0% DoD the total number of completed cycles decreases by almost 10 times for the cells with both AC3 concentrations. It can be assumed that the processes taking place in the cells with AC3 carbon on cycling are similar to those described above for the cells with TDA carbon additive.

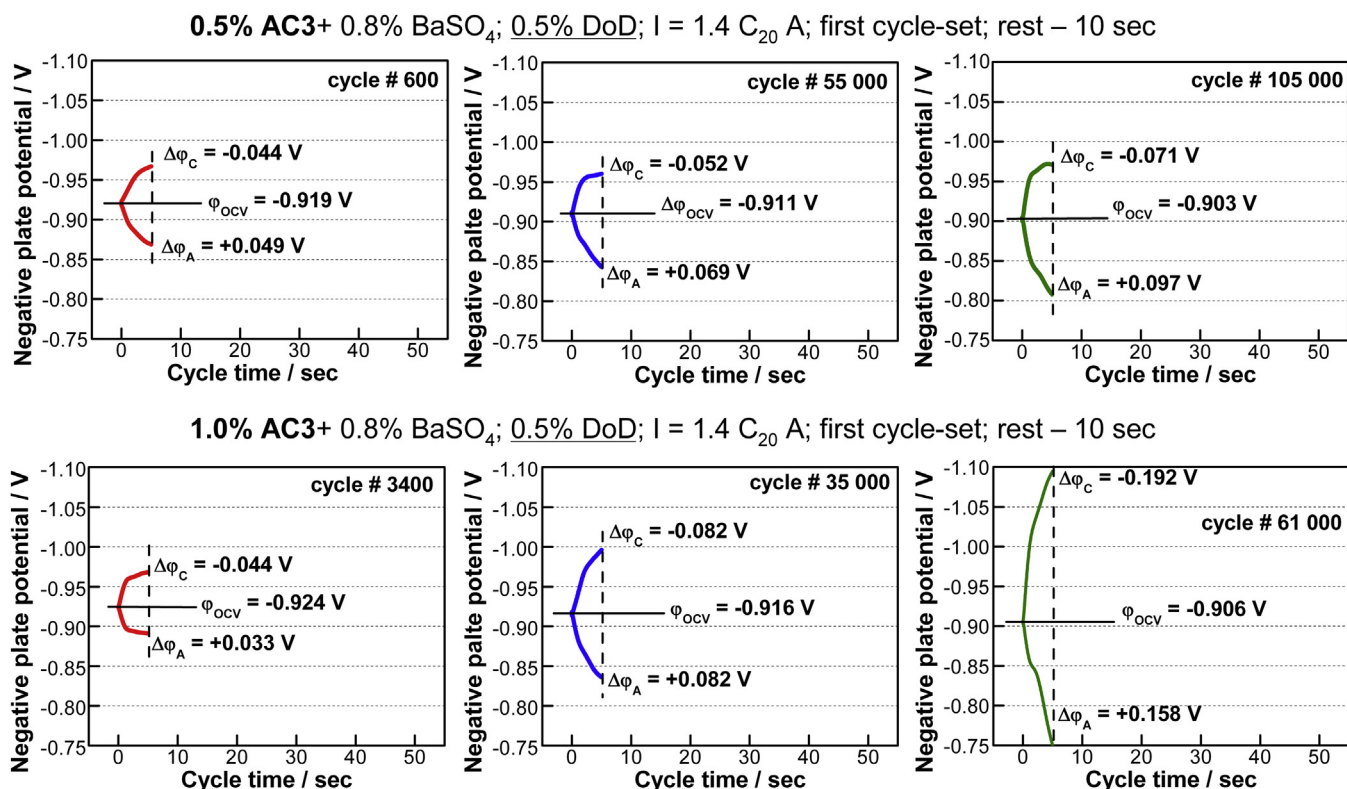


Fig. 15. Changes in negative plate potential within one micro-cycle as a function of polarization time for cells with 0.5 wt% or 1.0 wt% AC3 in NAM cycled at 0.5% DoD; at the beginning, in the middle and at the end of the first cycle-set.

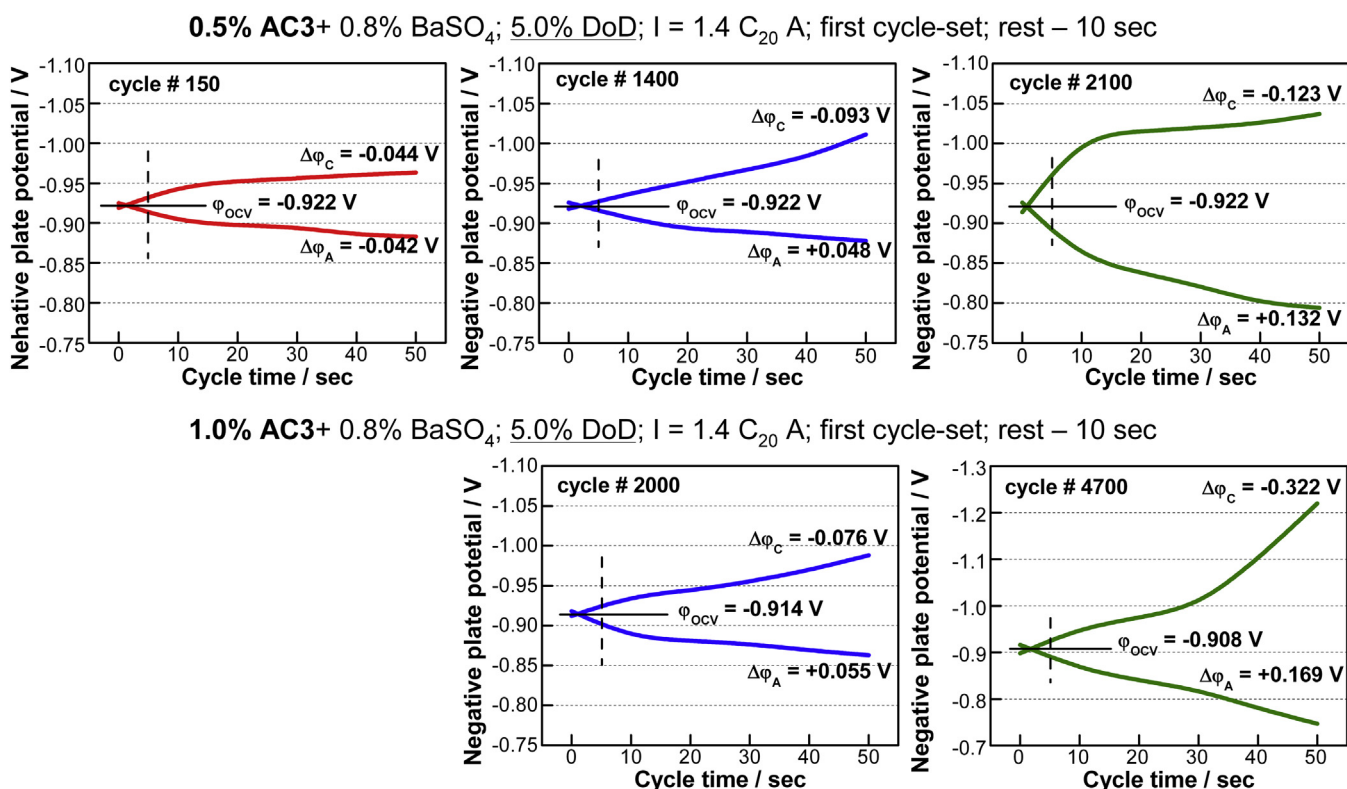


Fig. 16. Changes in negative plate potential within one micro-cycle as a function of polarization time for cells with 0.5 wt% or 1.0 wt% AC3 in NAM cycled at 5.0% DoD; at the beginning, in the middle and at the end of the first cycle-set.

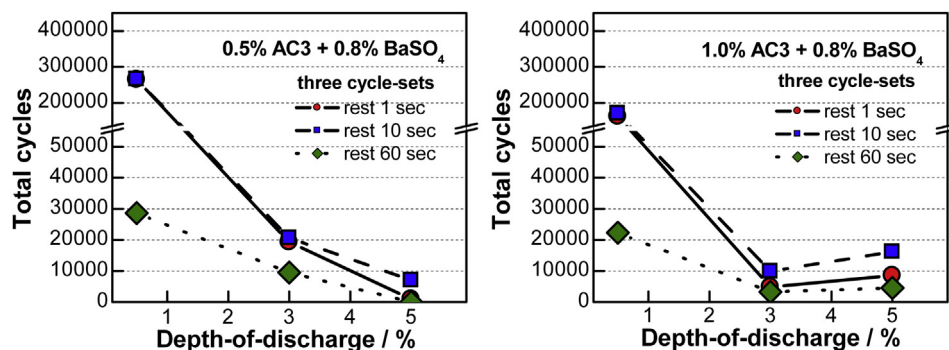


Fig. 17. HRPSoC cycling test results for cells with 0.5% or 1.0% AC3 carbon in NAM at three different depths of discharge.

The test cells with both AC3 concentrations in NAM exhibit the best cycleability when cycled at 0.5% DoD. The cells with 0.5 wt% AC3 complete a total of 266,000 cycles against 170,000 cycles (i.e. 35% less) for the cell with 1.0 wt% AC3. Why does the cycleability of the cells with higher AC3 load decline despite the fact that this carbon expands the specific NAM surface from $4.70 \text{ m}^2 \text{ g}^{-1}$ (at 0.5 wt% AC3) to $8.78 \text{ m}^2 \text{ g}^{-1}$ (at 1.0 wt% AC3)? Most probably, this carbon additive alters the pore system and structure of the negative active mass and thus influences the reversibility of the processes on cycling and hence the number of completed cycles.

Fig. 18 presents the results of the simulated HRPSoC cycling tests for cells with 0.5 wt% or 1.0 wt% AC3 carbon black in NAM, cycled at three different DoD and three different rest period times. The figure summarizes the data for the number of completed HRPSoC cycles per cycle-set.

With this carbon additive, too, the general tendency observed is a decline in cycleability from cycle-set to cycle-set. The degree of this decline depends on the depth of discharge, the duration of the rest periods and the carbon content in NAM. When cycled at 0.5% DoD with 10 s rest periods, the cells with 0.5 wt% AC3 in NAM complete 110,000 cycles within the first cycle-set against only 60,000 cycles in the third cycle-set. At 5.0% DoD again, the best cycleability is observed when the cells are cycled with 10 s rest periods between the charge and discharge pulses.

3.4.4. Structure of NAM with AC3 carbon black after 3 cycle-sets of the HRPSoC cycling test

Fig. 19 shows SEM images of NAM samples taken from the surface and from the inner layers of plates with 0.5 wt% AC3 carbon black. When cycled at 0.5% DoD, the macrostructure of the negative active mass differs but slightly across the plate thickness. At this DoD, the lead particles formed on the surface are a bit larger in size than those in the bulk of NAM. The pore system is pretty much the same in the two NAM zones.

This is not the case with the plates cycled at 3.0% or 5.0% DoD, however. Here, the surface NAM layers differ significantly in macrostructure from the bulk of NAM. Aggregates of lead particles with macropores inbetween can be seen in the surface NAM layers. These are not so well-defined as the aggregates observed in Fig. 12. Obviously, the nano-sized carbon particles adsorbed onto the surface of the lead crystals prevent the formation of well pronounced aggregates. With this carbon additive, too, the structure of the surface NAM layers is built of small lead particles interconnected into big aggregates, whereas the lead particles formed in the inner plate zones are bigger in size when the cells are cycled at 3.0% or 5.0% DoD.

The SEM images in Fig. 20 show the structure of the negative active mass containing 1.0 wt% AC3 carbon black. A tendency to

equalization of the macrostructure in the two NAM zones is observed.

Based on the SEM data in Figs. 11 and 12, and Figs. 19 and 20 it can be concluded that carbon additives to NAM alter the latter's macrostructure in different ways, depending on carbon particle size and their affinity to lead.

Fig. 21 shows SEM pictures (at lower magnification) of NAM samples from the inner zones of plates with 1.0 wt% AC3 after cycling at: (a) 0.5% DoD and (b) 3.0% DoD. Large void spaces (caverns) can be seen in the bulk of NAM. Probably, during formation of the plates and during their re-charge after the capacity tests, some hydrogen has evolved in the plate interior which has displaced the lead crystals thus forming large gas spaces between them. These results indicate that the AC3 nano-particles adsorbed on the surface of the lead crystals impart a certain flexibility to the NAM structure, which allows this displacement of its particles without cracking or destroying it.

3.4.5. Phase composition of NAM with AC3 carbon black after three cycle-sets of the HRPSoC cycling test

The XRD patterns in Fig. 22 are for NAM samples with 0.5 wt% AC3 carbon black cycled at three different depths of discharge, 0.5%, 3.0% or 5.0% DoD. The experimental data in the figure evidence the presence of considerable amounts of tet-PbO (α -PbO) beside the PbSO₄ phase. The shape of the characteristic peak at $2\theta = 28.6^\circ$ suggests that the tet-PbO phase is composed of very small crystallites.

On cycling at 5.0% DoD, more tet-PbO is formed in NAM than when cycled at 3.0% or 0.5% DoD. Actually, the tet-PbO content is commensurable with the content of PbSO₄, which indicates that the electrochemical oxidation of Pb in H₂SO₄ solution involves not only a chemical process of formation of PbSO₄, but also a chemical process of tet-PbO formation as well. The latter phase can only be formed in alkaline medium. So the question arises: How is the solution in the pores of NAM alkalized?

Fig. 23 shows the obtained X-ray diffractograms for NAM with 1.0 wt% AC3 after cycling at 0.5%, 3.0% or 5.0% DoD, followed by re-charge of the cells.

The XRD data evidence that the highest amount of tet-PbO in the negative active mass is formed when cycling is conducted with 5 s pulses (0.5% DoD). The PbSO₄ content is low after the re-charge. With increase of the DoD to 3.0% the amount of tet-PbO strongly decreases, but the PbSO₄ content is low, too. Probably, both phases have been greatly reduced during the re-charge of the cell after the 3rd cycle-set. On cycling at 5.0% DoD, followed by cell re-charge, the main crystal phase remaining in the NAM is lead sulfate. No diffraction peaks for tet-PbO are observed in the diffractogram. The diffraction peaks for PbSO₄ are higher than that of metallic lead, which indicates that a thick PbSO₄ layer has formed.

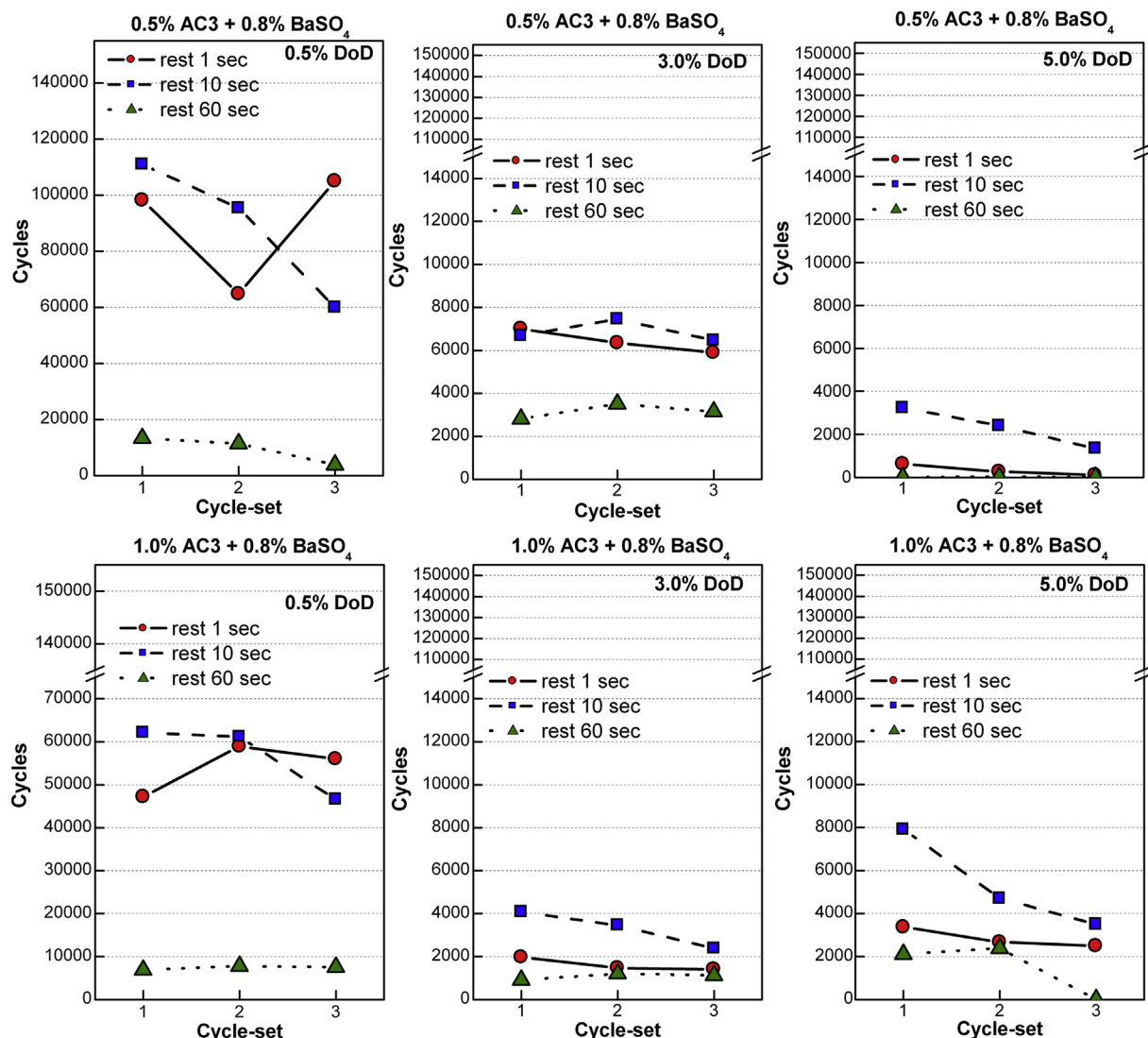


Fig. 18. Completed cycles per cycle-set for cells with 0.5 wt% or 1.0 wt% AC3 in NAM cycled at three different depths of discharge: 0.5%, 3.0% or 5.0% DoD.

3.4.6. Mechanism of formation of tet-PbO in the pores of NAM

Formation of PbO on anodic polarization of Pb electrode immersed in H_2SO_4 solution was established by Lander [14] and Burbank [15] employing XRD analysis.

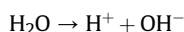
We studied these processes, too, and proposed the following mechanism of formation of tet-PbO [16–19]. Pores of membrane sizes form in the anodic layer built of lead sulfate crystals. The access of the big SO_4^{2-} and HSO_4^- ions into the membrane-sized pores is impeded. When the electrochemical reaction of formation of Pb^{2+} proceeds, to sustain the solution in the membrane-sized pores electroneutral, H^+ ions migrate from the pores to the bulk solution, which results in alkalization of the solution in the pores and formation of PbO [16–19]. Later, Ruetschi confirmed experimentally the membrane properties of chemically precipitated BaSO_4 and PbSO_4 layers [20].

Let us assume that the above mechanism of formation of PbO in NAM is initiated when the carbon additive in NAM reduces the latter's pores to membrane sizes. What processes take place in NAM according to the above mechanism?

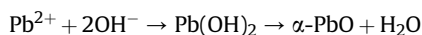
The porometric data for the different NAM samples give mean pore radius values of $1.10 \mu\text{m}$ for the NAM with 0.5 wt% AC3 carbon additive and $0.55 \mu\text{m}$ for 1.0 wt% AC3 content, respectively. The transport of ions in narrow pores is impeded and thus the pores

act as a semi-permeable membrane for the ionic transport (Fig. 24b). SO_4^{2-} and HSO_4^- ions are relatively big in size and less mobile. Their movement through pores with radii smaller than $1.0 \mu\text{m}$ may be impeded.

When anodic current flows through the cell, an electrochemical reaction of Pb^{2+} ion formation proceeds in the pores (Fig. 24c). These ions charge the solution in the pores with positive charges. In order to neutralize these positive charges, SO_4^{2-} ions have to diffuse from the bulk solution to the NAM pores. However, their access to the pores is impeded, so the solution in the pores remains positively charged. Its electroneutralization involves dissociation of water in the pore solution (Fig. 24d):



Under the action of the electric field in the pores, H^+ ions migrate from the NAM pores to the bulk solution (Fig. 24d). The remaining OH^- ions increase the pH of the solution in the pores to alkaline values. A reaction between Pb^{2+} and OH^- ions starts, producing $\text{Pb}(\text{OH})_2$ and PbO (Fig. 24e):



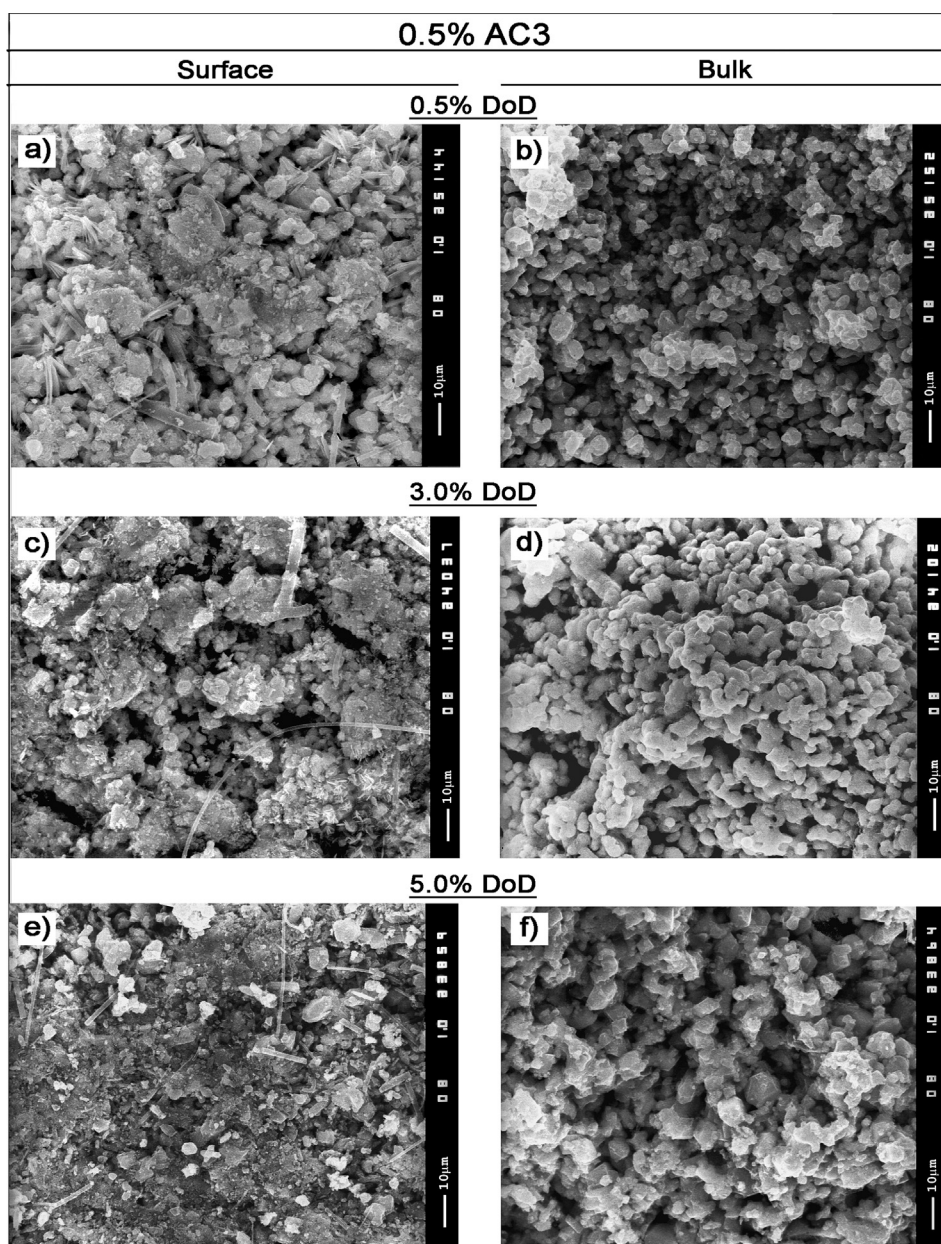


Fig. 19. Structure of NAM with 0.5 wt% AC3 after cycling at 0.5%, 3.0% or 5.0% DoD. (a, c, e) NAM surface layer; (b, d, f) NAM sample from plate interior.

Tetragonal PbO (i.e. α -PbO) precipitates onto the pore surface. Thus, despite that the lead active mass is in contact with H_2SO_4 solution, the impeded transport of SO_4^{2-} ions and their inability to move freely through the membrane-sized pores cause the pH of the pore solution to rise and create conditions for a reaction of α -PbO formation to proceed at the negative plates of the lead–acid cell. This phenomenon is a result of the impact of carbon particles on the structure of the negative active mass.

3.5. Elementary processes taking place at the negative plates of lead–acid cells with different carbon additives in NAM on HRPSoC cycling

The obtained results from the HRPSoC cycling tests of cells with TDA active carbon or AC3 carbon black added to NAM give us grounds to conclude that three types of processes occur in the cells when polarized for up to 60 s as follows:

- Capacitive charging and discharging of the electric double layer formed on the surface of NAM. These processes exhibit only when the lead active mass contains high specific surface carbon powder.
- Electrochemical oxidation of lead and formation of PbSO_4 . Dissolution of PbSO_4 and electrochemical reduction of Pb^{2+} ions to Pb.
- Recrystallization of the small PbSO_4 particles into big PbSO_4 crystals and partial sulfation of the negative plates. These processes occur when the negative plates are not fully charged.

These processes will be discussed in more detail below.

3.5.1. Capacitive processes of charging and discharging of the interface carbon-doped NAM/electrolyte on cycling with up to 5 s high current pulses

An electric double layer forms on the lead and carbon surfaces during charge, comprising a compact (Helmholtz) layer and a

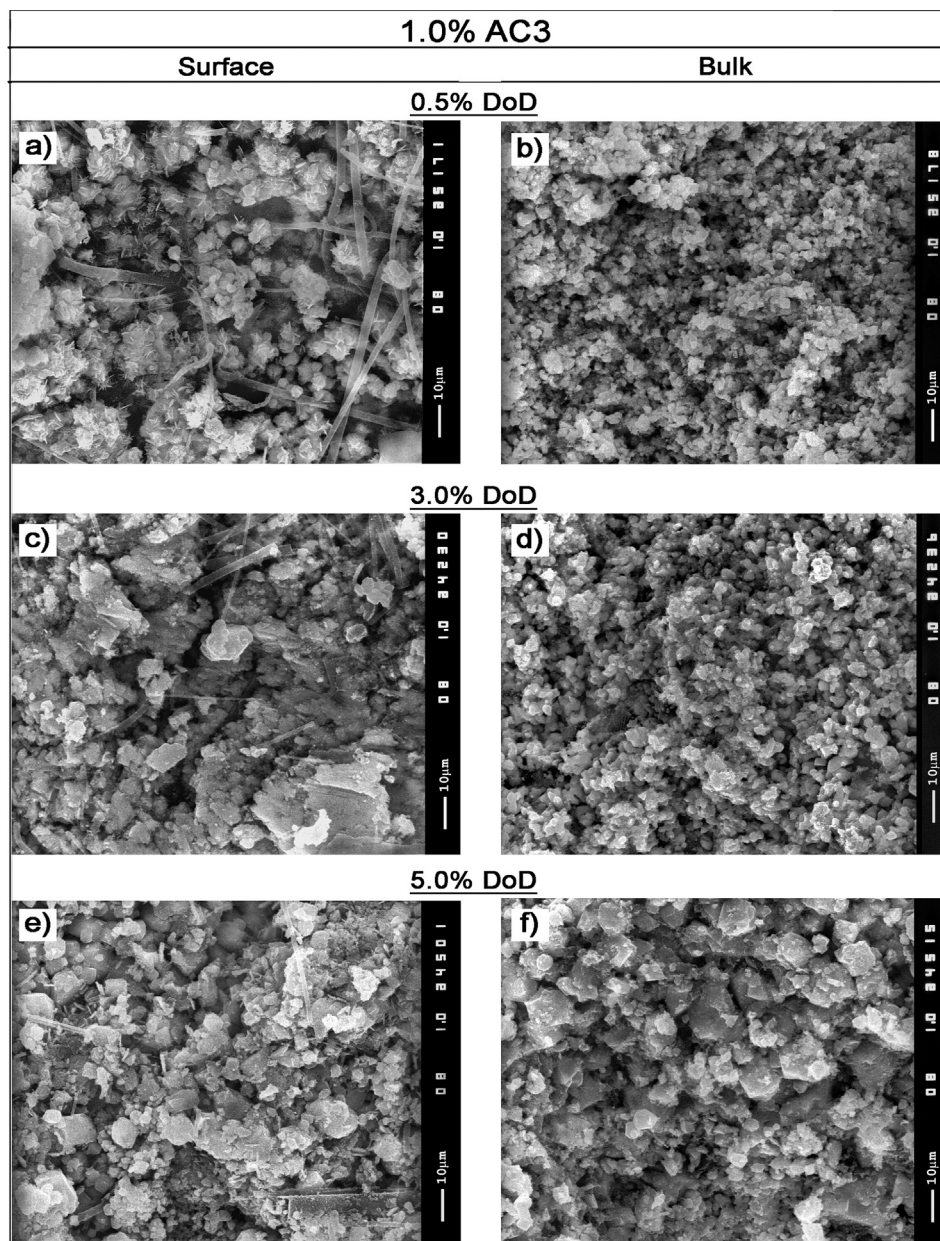


Fig. 20. Structure of NAM with 1.0 wt% AC3 after cycling at 0.5%, 3.0% or 5.0% DoD. (a, c, e) NAM surface layer; (b, d, f) NAM sample from plate interior.

diffuse layer. Fig. 25 shows a schematic representation of the electric double layer on the electrode surface charged with positive and negative electric charges. The thickness of the diffuse region of the electric double layer depends on the concentration of ions in the solution: the lower the ion concentration, the thicker the diffuse layer. In our case, the sulfuric acid concentration is high and hence a very thin diffuse layer will form, which would hardly affect the processes on the electrode surface.

Within one micro-cycle, the carbon and lead surfaces are charged with positive and negative electric charges. Hence, the ion concentration (H^+ or SO_4^{2-} ions) in the compact Helmholtz layer will change. These are fast processes and can be explained by the following mechanism. H^+ ions are six times faster than SO_4^{2-} ions. When the carbon and lead surfaces are positively charged, H^+ ions are pushed by the electric field out of the compact Helmholtz layer into the bulk solution. The positive

charge of the electrode surface is neutralized by the remaining SO_4^{2-} ions. When the carbon and lead surfaces are charged with negative charges, the H^+ ions rapidly occupy sites in the compact Helmholtz layer and thus neutralize the electric charges of the electrode surface. Since electroneutralization of the electric double layer involves movement of H^+ ions, the charge–discharge processes of the electric double layer proceed at a high rate, which is actually observed on cycling with high current pulses of 5 s duration.

The results in Figs. 9 and 17 indicate that charging and discharging of the electric double layer proceed very quickly and Fig. 10 evidences that they are reversible. If the battery is required to operate with high reversibility of the charge–discharge processes and hence have high cycleability per cycle-set, the negative active material should contain a certain amount of a particular carbon additive.

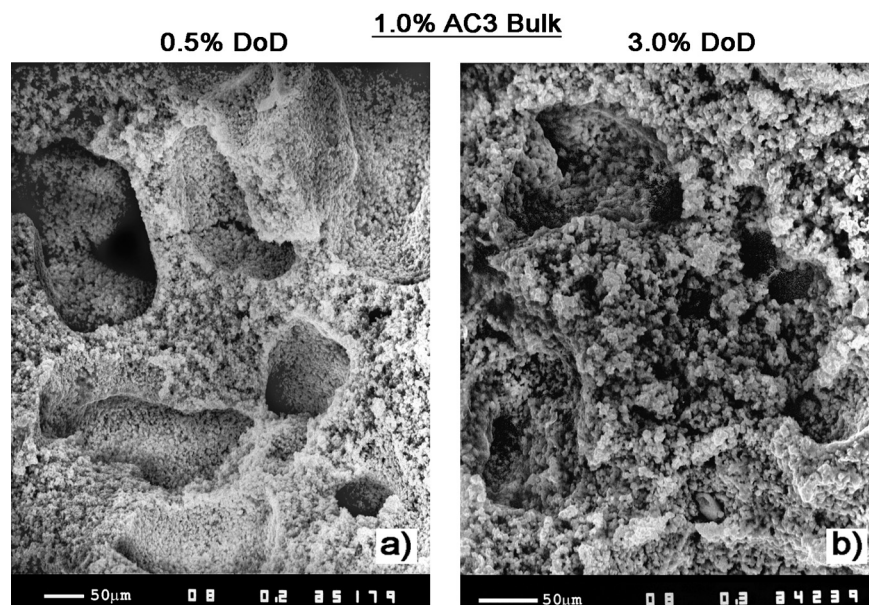
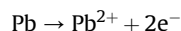


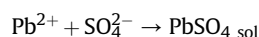
Fig. 21. SEM images at lower magnification of the bulk of NAM with 1.0 wt% AC3 carbon black after cycling at 0.5% or 3.0% DoD.

3.5.2. Electrochemical and chemical reactions on anodic and cathodic polarization of the negative electrodes within one micro-cycle of the HRPSoc cycling test

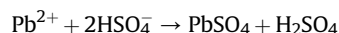
During the anodic current pulse applied to the negative plates of a lead–acid cell, when the oxidation potential of lead is reached, an electrochemical reaction of lead oxidation starts on the electrode surface:



The concentration of Pb^{2+} ions increases and, above a certain oversaturation level, a chemical reaction proceeds between these ions and SO_4^{2-} ions from the solution, as a result of which PbSO_4 molecules are formed at the electrode surface:

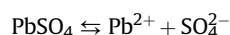


or

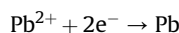


These PbSO_4 molecules diffuse to the solution near the electrode surface and along the electrode surface, and get incorporated into the crystal lattice of the already formed PbSO_4 nuclei and crystals they come across. The newly formed PbSO_4 phase covers part of the carbon and lead surfaces, thus reducing the electrochemically active surface. To sustain constant current, the polarization of the plate increases. The presence of carbon in the negative active material provides additional surface on which PbSO_4 can be formed, thus retarding accumulation of PbSO_4 phase on the lead surface and hence the capacity of the negative plates increases.

Depending on their solubility lead sulfate crystals sustain a definite concentration of Pb^{2+} ions in the solution



After the anodic pulse, the plates are polarized cathodically. The electrode surface is charged with negative electric charges. Above a certain negative potential, the electrochemical reaction of reduction of the Pb^{2+} ions starts:



Pb^{2+} ions are reduced on both the lead and carbon surfaces but at different rates. As a result of the above reaction local undersaturation with Pb^{2+} ions is created at certain sites on the electrode surface and hence diffusion of Pb^{2+} ions starts to these sites on the lead or carbon surfaces, where they are reduced electrochemically to Pb atoms. Thus, a lead phase grows both on the lead and carbon surfaces.

The HRPSoc cycling test results presented in Figs. 9, 10, 17 and 18 evidence a reduction in the total number of micro-cycles achieved, when the depth of discharge is increased from 0.5% to 3.0% or 5.0%. Under such conditions, considerable amounts of PbSO_4 crystals remain unreduced and the electrochemically active electrode surface decreases. The accumulation of lead sulfate crystals on the electrode surface leads to progressive sulfation of the electrode. The rate of this sulfation depends on two parameters: the duration of the current pulses and the time of rest between them.

The obtained experimental data suggest that there is an optimum configuration of the capacitive, electrochemical and chemical processes on HRPSoc cycling, which ensures maximum number of completed charge–discharge cycles. This optimum configuration depends on the type of carbon additive in NAM and is determined by the electrochemical electrode system. This effect is more clearly exhibited with the TDA activated carbon and less so with the AC3 carbon black.

The above discussed experimental results indicate that the processes in the carbon (capacitive) and lead (electrochemical) electrode systems are interrelated and have a mutual effect on each other, but when the electrochemical system starts operating, its impact on the electrode behavior becomes dominating.

3.5.3. Comparison between the electrochemical and capacitive electrode systems formed on the negative plates

Fig. 26 presents an electric circuit model of a lead–acid cell with Pb–C electrodes. The negative plates comprise two systems: a capacitive (C) and an electrochemical (EC) one. The positive plate is common for the two systems. The capacitive and electrochemical systems operate in parallel and exert an impact on each other.

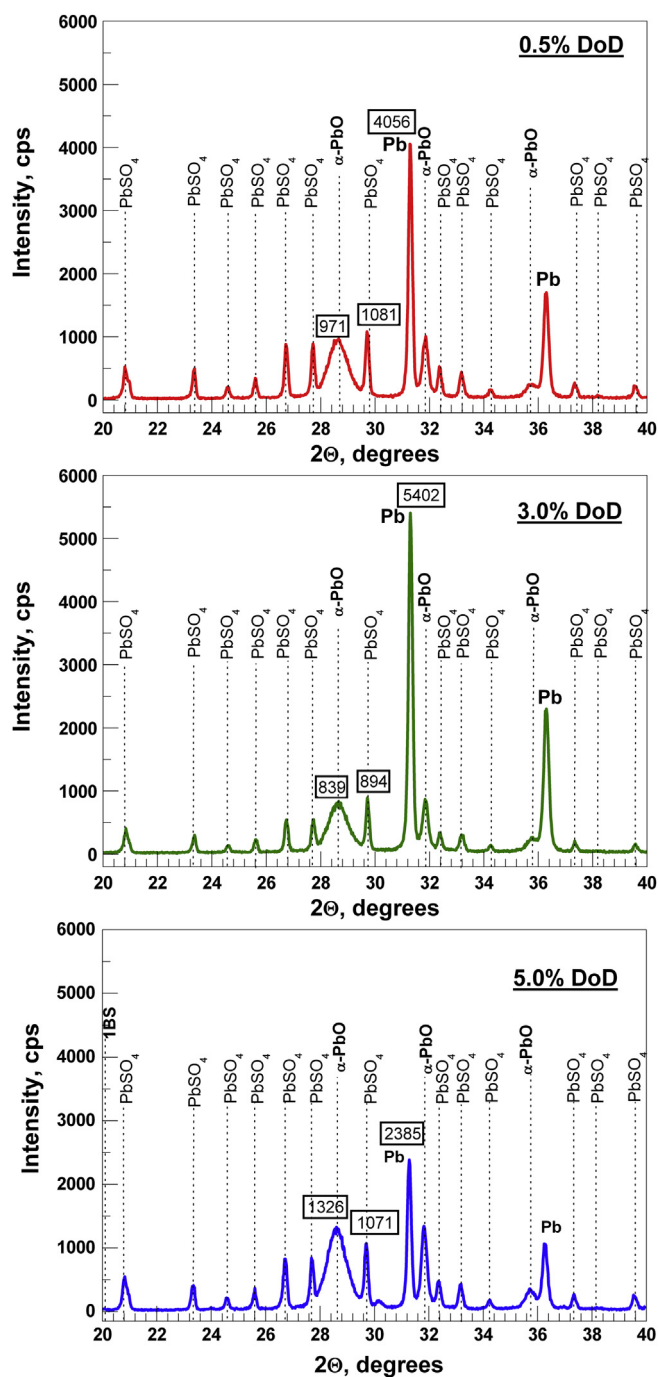


Fig. 22. X-ray diffraction patterns for the negative active mass with 0.5 wt% AC3 carbon black after cycling at 0.5%, 3.0% or 5.0% DoD.

What is the proportion between the Ah capacities of these two systems?

If we assume that the current flowing through the cell is consumed only for charging and discharging the capacitive system of the negative plates, then the quantity of electricity that passes within the 5 s pulses of charge and discharge will be 0.0097 Ah. Related to the total cell capacity of 4.5 Ah, the capacitive system contributes only 0.22% to the Ah capacity of the cell within one 5 s pulse within one micro-cycle. This estimate, though only a rough one, indicates that the electrochemical system formed on the negative plate has a dominating role in the charge–discharge processes and will determine the plate's behavior on cycling. Therefore, there is no Ah

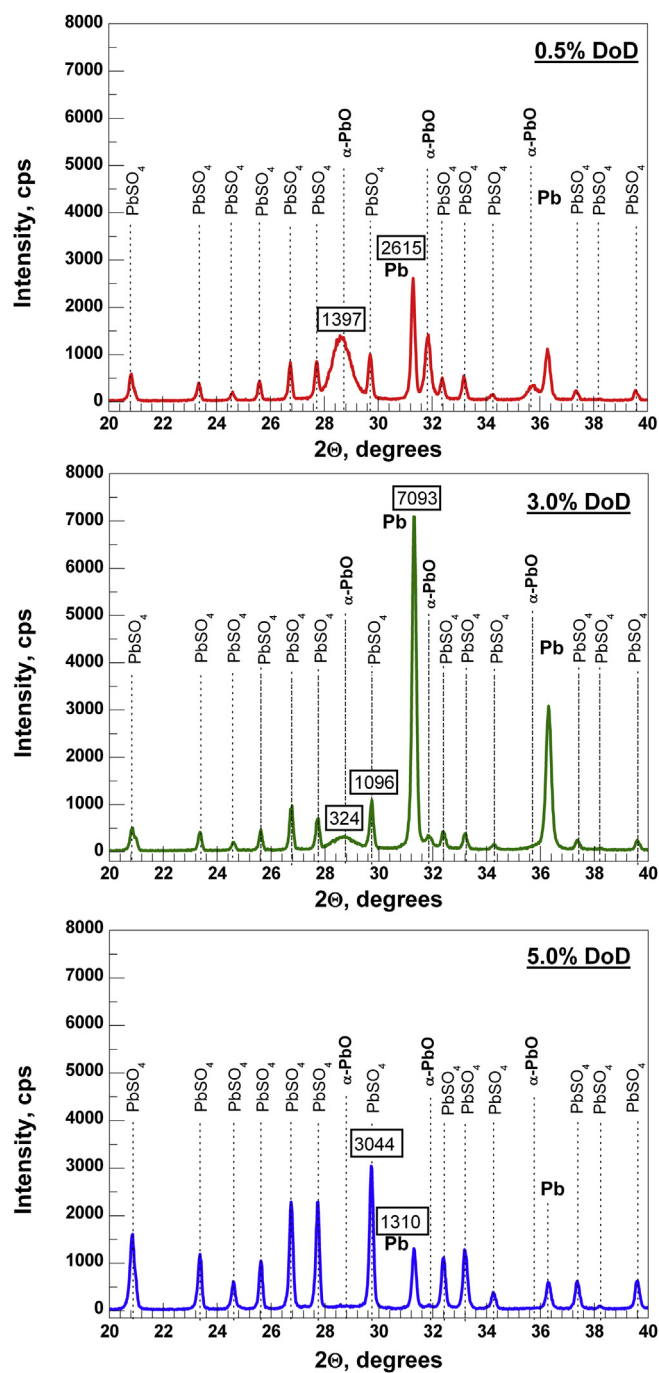


Fig. 23. X-ray diffraction patterns for the negative active mass with 1.0 wt% AC3 carbon black after cycling at 0.5%, 3.0% or 5.0% DoD.

equivalence between the lead and the carbon electrode systems despite the high surface of the latter. When electric current flows through the electrode, the carbon electrode system participates with its surface only, whereas the lead system involves considerable part (30–40%) of the lead volume.

The Ah capacity of the capacitive system on the negative plate depends on the specific surface of the negative active mass. In two previous studies of ours, we have established the correlations between NAM specific surface area and number of completed HRPSoC cycles, on the one hand, and the content of TDA or AC3 carbon additives in NAM, on the other hand [9,11]. Fig. 27 presents these correlations.

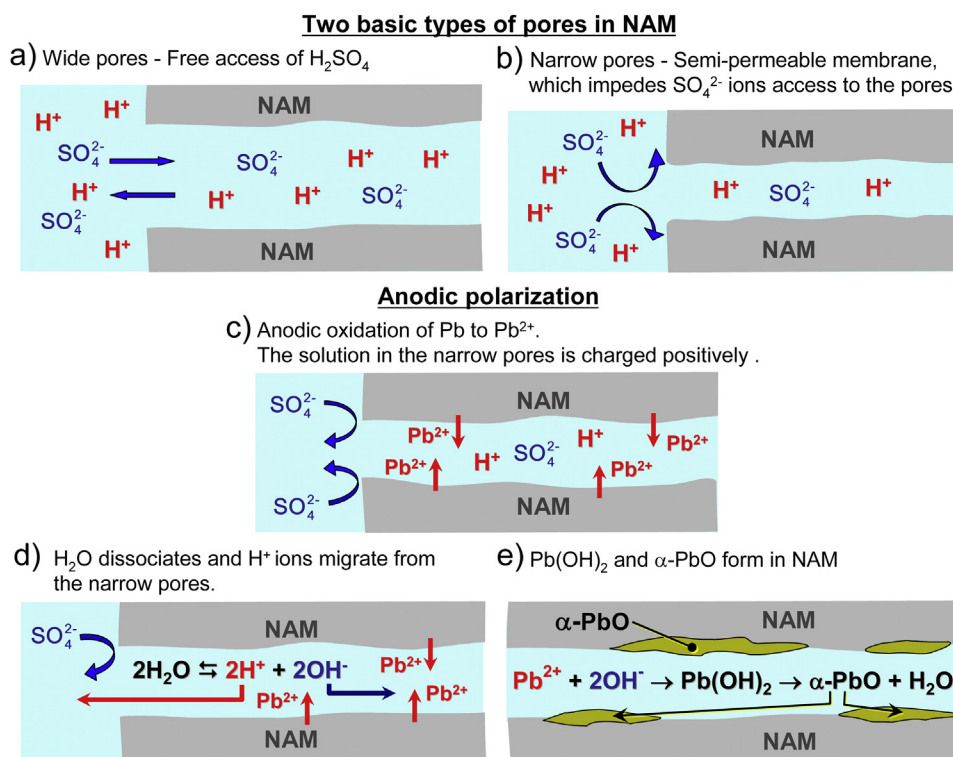


Fig. 24. Model scheme of the processes leading to alkalization of the solution in NAM pores and PbO formation.

The data in Fig. 27a, b show that higher loads of TDA activated carbon in NAM expand the latter's specific surface area which reaches a value of $25.20 \text{ m}^2 \text{ g}^{-1}$ at 2.0 wt% TDA loading level. The number of completed HRPSoC cycles per cycle-set (which is an indication of the reversibility of the charge–discharge processes) increases with increase of the TDA content in NAM to reach a stationary value at 1.0 wt% TDA, despite that the NAM surface increases further.

The graphs in Fig. 27c, d evidence an increase in NAM specific surface area with increase of the content of AC3 carbon black to reach a value of $20 \text{ m}^2 \text{ g}^{-1}$ at 2.0 wt% AC loading level. The cycleability per cycle-set increases abruptly from 900 cycles for cells with no AC3 to 9200 cycles for cells with 0.2 wt% AC3, but then declines with further increase of the carbon content down to 2700 cycles at 2.0 wt% AC3 in NAM. These experimental data indicate that AC3 carbon black improves significantly the reversibility of the charge–discharge processes when added in low concentrations to NAM.

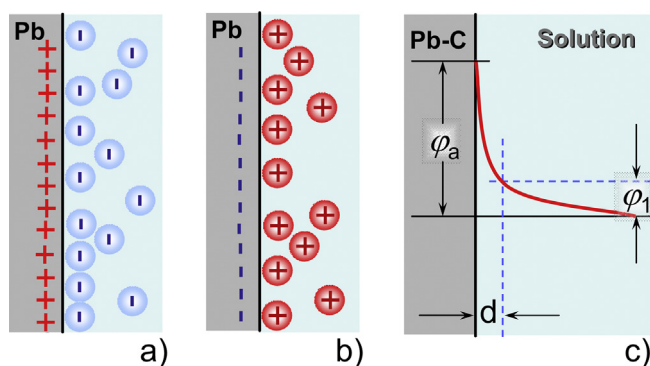


Fig. 25. Electric charge and potential distribution in the electric double layer on the electrode surface: (a) when positively charged and (b) when negatively charged.

The data in Fig. 27 confirm the assumption that the role of carbon in the negative plates is not confined only to its contribution to the electrical capacity of the plates. Carbon additives change the pore system and the overall behavior of the negative plates, thus inducing changes in the electrochemical system as well.

Because of this strong effect of carbon additives on the behavior of the negative plates, these plates, resp. the cells (batteries) with carbons added to NAM, have to be called *lead–carbon electrodes*, resp. *lead–carbon cells (batteries)*. Not all carbon materials are suitable for use as additives to the negative plates of lead–acid batteries so as to ensure appropriate behavior of the negative active mass that would meet fully the requirements for HEV batteries.

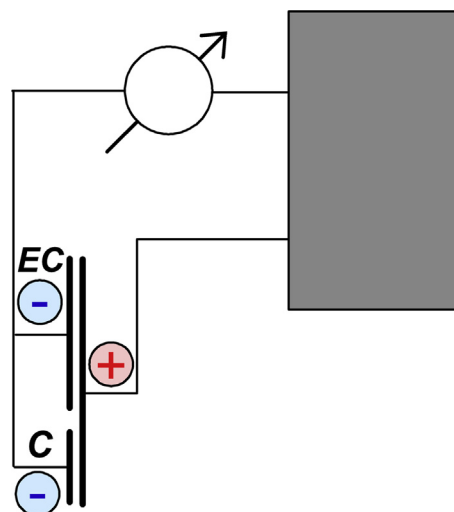


Fig. 26. Electric circuit model of a lead–acid cell with capacitive (C) and electrochemical (EC) electrode systems.

3.5.4. Processes of sulfation of the negative plates

The solubility of lead sulfate crystals depends on their size. The equilibrium concentration of Pb^{2+} ions in the solution is determined by the Ostwald–Freundlich equation:

$$\ln(C_{\text{Pb}^{2+}}/C_{\text{Pb}^{2+}}^{\infty}) = K/T \cdot r$$

where, $C_{\text{Pb}^{2+}}$ is the Pb^{2+} ion concentration over small PbSO_4 crystals, $C_{\text{Pb}^{2+}}^{\infty}$ is the Pb^{2+} ion concentration over big PbSO_4 crystals, K is a constant, T is temperature; r is the radius of PbSO_4 crystals.

The kinetics of PbSO_4 recrystallization has been investigated earlier [21]. Following the reaction between $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ and H_2SO_4 , which results in formation of PbSO_4 crystals, the changes in concentration of the lead sulfate molecules in the solution with time are monitored. The obtained results are presented in Fig. 28.

At the beginning, the concentration of PbSO_4 molecules in the solution is high due to the high solubility of the small PbSO_4 crystals, but then decreases rapidly as a result of the recrystallization process. After 96 hours, the PbSO_4 concentration reaches a stationary value. The following processes occur within this period.

Big PbSO_4 crystals are in a state of oversaturation and PbSO_4 molecules have to precipitate to restore the equilibrium concentration of Pb^{2+} ions (or PbSO_4 molecules) in the solution near the big PbSO_4 crystals. On the contrary, small PbSO_4 particles are in a state of undersaturation and they have to dissolve to restore the equilibrium concentration of Pb^{2+} ions (or PbSO_4 molecules) in the solution. The smallest PbSO_4 particles determine the concentration of Pb^{2+} ions (or PbSO_4 molecules). The big lead sulfate crystals grow at the expense of dissolution of the small ones.

In the present experiment, the negative electrodes are discharged to 50% state-of-charge prior to cycling. Thus, conditions are created for the process of recrystallization of the PbSO_4 crystals formed during the preliminary discharge. The data in Figs. 22 and 23 indicate that more PbSO_4 crystals are formed when cycling is

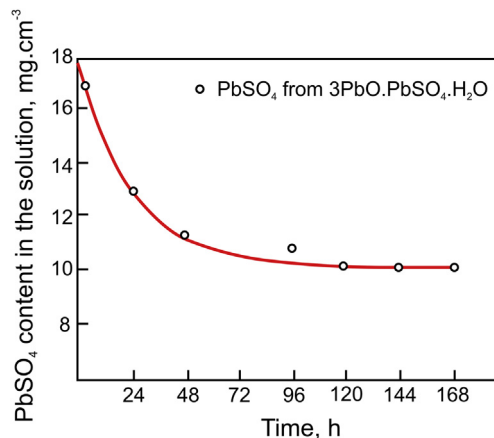


Fig. 28. Changes in PbSO_4 concentration with time of stay in 1 M H_2SO_4 solution [21].

conducted with 50 s charge and discharge pulses than on cycling with 30 s pulses. The longer time of discharge allows the processes of PbSO_4 crystal growth to progress to a more advanced stage and thus bigger lead sulfate crystals are formed. These crystals are more difficult to reduce during the re-charge of the cells and they are detected by the X-ray diffraction method.

To retard negative plate sulfation the rate of lead sulfate recrystallization should be slowed down. We have established that addition of definite amounts of poly-aspartic acid to the negative active material impedes lead sulfate crystal growth and improves the reversibility of the processes on HRPSoc cycling [22]. Most probably, there are other substances, too, which can act as inhibitors of PbSO_4 recrystallization and improve the charge acceptance of the negative plates. In this way, the adverse effect of the low battery state-of-charge on HEV cycling can be mitigated

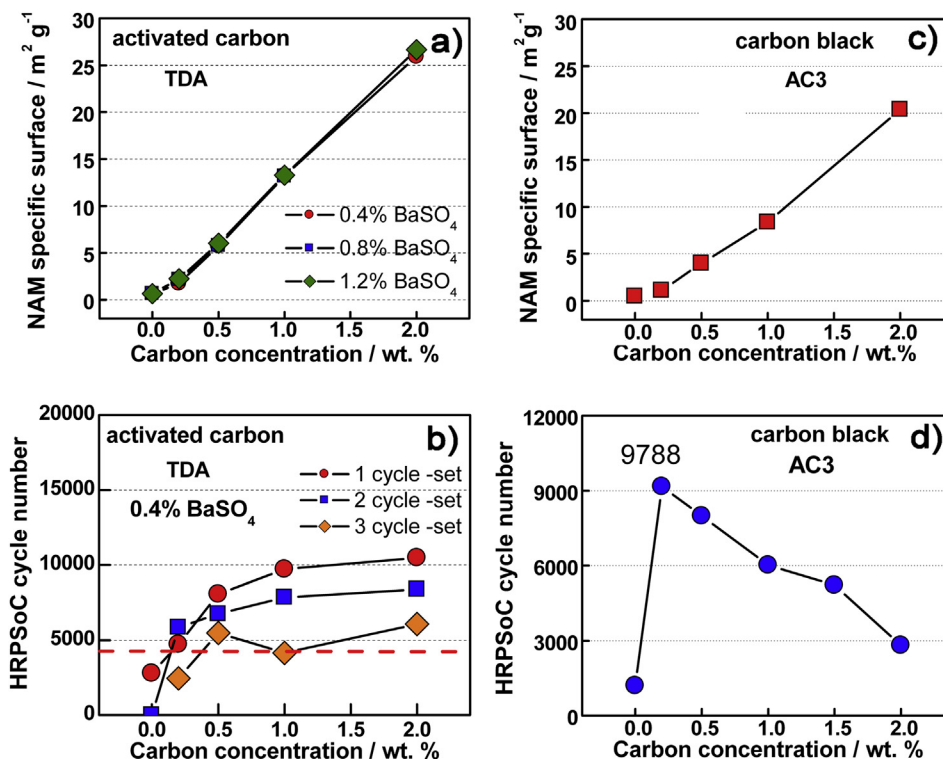


Fig. 27. Correlations between NAM specific surface area and number of completed HRPSoc cycles versus content of TDA or AC3 carbon additives in NAM [9,11].

through the use of such inhibitors of lead sulfate recrystallization. Thus, minor changes of the technology of negative plate manufacture could lead to significant improvement in the performance of lead–acid batteries for hybrid electric vehicle applications.

4. Conclusions

- When cells with carbon additives in NAM are cycled with 5 s charge and discharge pulses, and 1 s rest periods, the dominating elementary processes are capacitive charging and discharging of the electric double layer formed on the electrode surface.
- On cycling with 30 s or 50 s pulses (i.e. at 3.0% or 5.0% depth of discharge) with 60 s rest periods between the charge and discharge pulses, the main processes that determine the electrical parameters of the cells are the electrochemical reactions of Pb oxidation (during discharge) and PbSO₄ reduction (during charge), and the chemical reactions of formation and dissolution of PbSO₄. The number of completed cycles within one cycle-set declines by several factors as compared to the cycleability of cells with capacitively charged and discharged negative plates.
- Thus, two parallel energetic systems are formed at the negative plate: a capacitive carbon system with small Ah capacity but high rate of operation, and an electrochemical lead system with high capacity but low rate of operation. There is an optimum proportion between these two systems which ensures high electrical performance of the negative plates.
- Carbons added to the negative active material are included in the structure of NAM in different ways and affect the cycling performance of the cells. TDA activated carbon particles are incorporated into the skeleton structure of NAM and contribute to the capacitive charging and discharging of the plates, thus improving the cycleability of the cells. The AC3 fine powder carbon black particles adsorb onto the surface of the lead particles and thus alter the structure of NAM and eventually reduce the number of completed micro-cycles per cycle-set.
- Carbon additives change the pore system of NAM. When the mean pore radius is smaller than 1 μm, the skeleton structure of NAM acts as a semi-permeable membrane impeding the access of SO₄^{2−} ions to the pores in the bulk of NAM. As a result of the reaction of electrochemical oxidation, Pb²⁺ ions are formed in the pores, charging the pore solution with positive charges. To restore its electro-neutrality, H⁺ ions migrate from the pore solution to the bulk electrolyte and the solution in the pores gets alkalized. Under these conditions, tetragonal-PbO forms in the pores which impedes significantly the reaction of lead oxidation. The experimental data for NAM with AC3 carbon black after cycling confirm the formation of membrane-sized pores and of tet-PbO in NAM.

- The present paper makes an overview of the elementary processes that take place at the negative plates on HRPSoc cycling which include: charging and discharging of the electric double layer, electrochemical and chemical reactions of lead oxidation and of lead sulfate reduction, as well as processes of recrystallization of PbSO₄ and sulfation of the negative plates. It is important to identify which of the above elementary processes are rate limiting in the different battery operating regimes and modify the technology of negative plate manufacture accordingly so that the negative plates would not limit the performance of the battery in the respective duty.

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References

- [1] K. Nakamura, M. Shiomi, K. Takahashi, M. Tsubota, J. Power Sources 59 (1996) 153–157.
- [2] M. Shiomi, T. Funato, K. Nakamura, K. Takahashi, M. Tsubota, J. Power Sources 64 (1997) 147–152.
- [3] P.T. Moseley, R.F. Nelson, A.F. Hollenkamp, J. Power Sources 157 (2006) 3–10.
- [4] A.F. Hollenkamp, W.G.A. Balasing, S. Lau, O.V. Lim, R.H. Newnham, D.A.J. Rand, J.M. Rosalie, D.G. Vella, L.H. Vu. ALABC project N1.2. Final report, in: Proceedings of Advanced Lead–Acid Battery Consortium, Research Triangle Park, NC, USA, 2002.
- [5] L.T. Lam, C.G. Phyland, D.A.J. Rand, D.G. Vella, L.H. Vu. ALABC project N3.1. Final report, in: Proceedings of Advanced Lead–Acid Battery Consortium, Research Triangle Park, NC, USA, 2002.
- [6] M. Fernandes, J. Valenciano, F. Trinidad, N. Munos, J. Power Sources 195 (2010) 4458–4469.
- [7] M. Calabek, K. Micka, P. Krivak, P. Baka, J. Power Sources 158 (2006) 864–867.
- [8] P.T. Moseley, J. Power Sources 191 (2009) 134–138.
- [9] D. Pavlov, T. Rogachev, P. Nikolov, G. Petkova, J. Power Sources 191 (2009) 58–75.
- [10] D. Pavlov, P. Nikolov, T. Rogachev, J. Power Sources 195 (2010) 4435–4443, and 4444–4457.
- [11] D. Pavlov, P. Nikolov, T. Rogachev, J. Power Sources 196 (2011) 5155–5167.
- [12] L.T. Lam, R. Louey, J. Power Sources 158 (2006) 1140–1148.
- [13] J. Furukawa, T. Takada, D. Mouma, L.T. Lam, J. Power Sources 195 (2010) 1241–1245.
- [14] J.J. Lander, J. Electrochem. Soc. 99 (1951) 213–219.
- [15] J. Burbank, J. Electrochem. Soc. 103 (1956) 87–91, and 104 (1956) 693–701.
- [16] D. Pavlov, Ber. Bunsen. 71 (1967) 398–404.
- [17] D. Pavlov, Electrochim. Acta 13 (1968) 2051–2061.
- [18] D. Pavlov, R. Popova, Electrochim. Acta 15 (1970) 1483–1491.
- [19] D. Pavlov, Electrochim. Acta 23 (1978) 845–854.
- [20] P. Ruetschi, J. Electrochem. Soc. 120 (1973) 331–336.
- [21] D. Pavlov, I. Pashmakova, J. Appl. Electrochem. 17 (1987) 1075–1082.
- [22] D. Pavlov, P. Nikolov, J. Electrochem. Soc. 159 (8) (2012) A1215–A1225.